Reduction in greenhouse gas and other emissions from ship engines: Current trends and future options

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ABSTRACT

The impact of ship emission reductions can be maximised by considering climate, health and environmental effects simultaneously and using solutions fitting into existing marine engines and infrastructure. Several options available enable selecting optimum solutions for different ships, routes and regions. Carbon-neutral fuels, including low-carbon and carbon-negative fuels, from biogenic or non-biogenic origin (biomass, waste, renewable hydrogen) could resemble current marine fuels (diesel-type, methane and methanol). The carbon-neutrality of fuels depends on their Well-to-Wake (WtW) emissions of greenhouse gases (GHG) including carbon dioxide (CO_2), methane (CH_4), and nitrous oxide emissions (N_2O). Additionally, non-gaseous black carbon (BC) emissions have high global warming potential (GWP). Exhaust emissions which are harmful to health or the environment need to be equally removed using emission control achieved by fuel, engine or exhaust aftertreatment technologies. Harmful emission species include nitrogen oxides (NO_x), sulphur oxides (SO_x), ammonia (NH_3), formaldehyde, particle mass (PM) and number emissions (PN). Particles may carry polyaromatic hydrocarbons (PAHs) and heavy metals, which cause serious adverse health issues. Carbon-neutral fuels are typically sulphur-free enabling negligible SO_x emissions and efficient exhaust aftertreatment technologies, such as particle filtration. The combinations of carbon-neutral drop-in fuels and efficient emission control technologies would enable (near-)zero-emission shipping and these could be adaptable in the short- to mid-term. Substantial savings in external costs on society caused by ship emissions give arguments for regulations, policies and investments needed to support this development.

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Nomenclature and abbreviations

%S	sulphur content in percent
BC	black carbon
Bio-FA	non-esterified fatty acid biofuel
BrC	brown carbon
BT	bubble towers
BTL	biomass-to-liquids
CCS	carbon capture and storage
CCU	carbon capture and utilization
CII	carbon intensity indicator
CNG	compressed natural gas
CO_2eq	carbon dioxide equivalent
Cslip	emissions of the fuel lost as fugitive emissions;
DF	dual-fuel
DM	distillate marine fuels
DME	dimethyl ether
DOC	diesel oxidation catalyst
DPF	diesel particulate filter
EC	elemental carbon
EEDI	energy efficiency design index
EEXI	energy efficiency existing ship index
EGR	exhaust gas recirculation
ESP	electrostatic precipitators
ETS	emission trading system
EV	electric vehicle
FAME	fatty acid methyl ester
FC	fuel cell
FSN	filter smoke number
FT	Fischer-Tropsch liquefaction
GHG	greenhouse gases
Gt	gigatons
GTL	gas-to-liquids
GWP	global warming potential
HP DF	high-pressure DF
HSD	high-speed diesel
HVO	hydrotreated oils and fats
ICCT	International Council on Clean Transportation
ICE	internal combustion engines
IMO	International Maritime Organisation
LBG	liquid biogas
LCFS	low carbon fuel standard
LII	laser-induced incandescence
LNG	liquefied natural gas
LOHC	liquid organic hydrogen carriers
LPDF	low-pressure DF
MAAP	multiangle absorption photometry
MCR	maximum continuous rating
MDO	marine diesel oil
MGO	marine gas oil
MOC	methane oxidation catalysts
MSD	medium speed diesel
NG	natural gas
NMHC	non- hydrocarbons
NO_x	nitrogen oxides
PAH	polyaromatic hydrocarbons
PAS	photoacoustic spectroscopy
PEMFC	proton exchange membrane fuel cells
PM	particulate matter emission
PN	particle number emission
PNnv	solid, non-volatile particle number
PNtot	total particle number
PPR	Sub-Committee on Pollution Prevention and Response
PVC	polyvinyl chloride
rBC	refractory BC
RED	renewable energy directive
SCR	selective catalytic reduction
SECA	emission control areas for SO_x
SOFC	solid oxide fuel cells
SO_x	sulphur oxides
SSD	slow speed diesel
TOA	thermal-optical analysis
TtW	tank-to-wheel
WES	wet electrostatic scrubber
WiFE	water-in-diesel fuel emulsions
VLSFO	very low sulfur fuel oil
WtW	well-to-wake

1. Background

Warning messages on climate change are becoming ever more serious and all possible actions are necessary for the shared endeavour to mitigate this threat. This also involves the maritime shipping sector. Of global trade, shipping represents approx. 80% by volume, and 70% by value [1]. In 2018, the global carbon dioxide (CO_2) emissions of shipping amounted to 1.06 gigatons (Gt) representing a share of 2.89% of global anthropogenic CO_2 emissions. Since 2008, the volume and CO_2 emissions from shipping have decoupled along with improved carbon intensity (mainly in attempts to save on fuel costs). However, in a range of scenarios, CO_2 emissions from shipping could increase in the absence of preventive actions [2,3]. An ambitious greenhouse gas (GHG) strategy by the International Maritime Organisation (IMO) aims to cut the shipping sector's carbon intensity by up to 40% by 2030 and 70% by 2050 compared to 2008. An even more challenging goal to achieve 100% carbon emission reduction by 2050 across sectors globally was set at the United Nations Climate Change Conference in 2021 [4]. In COP26, the Clydebank Declaration initiative was signed by 19 countries to build at least six decarbonised "green corridors" for zero-emission vessels by 2025 [5]. The IMO aims to help increase the energy efficiency of ships by measures such as an Energy Efficiency Design Index (EEDI), Energy Efficiency Existing Ship Index (EEXI) and carbon

intensity indicator (CII). Regional targets and regulations have also been set, for example, the FuelEU Maritime Initiative in the EU Green Deal "Fit for 55" package (14 July 2021) proposing a maximum limit on the GHG intensity of energy used on-board by ships. The Fit for 55 package also suggests shipping to be included in the EU's Emission Trading System (ETS) [6]. Investments in climate-neutral shipping are supported by the Poseidon Principles, Getting to Zero Coalition (deep-sea zero-emission vessels and infrastructure), and the European Sustainable Shipping Forum (greener technologies). The European Commission has also introduced the Inducement Prize for the Promotion of Renewable fuels in retrofitted container ships [7].

Of GHG emissions, CO_2 is the most important contributor to global warming, while important gaseous contributors also include methane (CH_4) and nitrous oxide (N_2O) emissions with 100-year global warming potentials (GWP100) of 28 and 265 times higher than that of CO_2, respectively [8]. However, the second important anthropogenic species contributing to global warming after CO_2 emission is non-gaseous black carbon (BC) emission with a GWP100 of 900 [9]. With the inclusion of BC emissions, the CO_2 equivalent (CO_2eq) emissions of shipping increase by 7% [3]. BC, and to a lesser extent brown carbon (BrC), is dark in colour and strongly absorbs light, thus warming the atmosphere as the light energy is converted to heat. The warming impact of BC emissions is significant, and especially so in the Arctic through its deposition on ice

and snow as the ice-free sailing season lengthens and allows a rise in ship traffic [10,11,12]. The residence time of BC in the atmosphere averaging around 7.3 days allows ship plumes to travel and to have an effect at a distance from the source [13]. The overall impact of shipping emissions on global warming will increase along with reducing sulphur oxide (SO$_x$) emissions and cooling aerosol species (sulphates and organics) if the climate-warming BC emissions remain [14–16]. The IMO has been working on BC emissions from international shipping since 2011 (MEPC 68).

Ship emissions are harmful, not only to climate but also to air quality, human health and the environment. Air pollution alone is estimated to cause approx. 6.5 million deaths annually [17]. Despite the 2020 marine fuel sulphur limit of 0.5%, shipping is estimated to account for approx. 250,000 premature deaths and 6.4 million childhood asthma cases annually [14] and also earlier evaluations estimated a high number of premature deaths caused by shipping annually [18–20]. Notably, ships sail and manoeuvre near densely inhabited coastal areas and cause local air quality problems near the coastline. Approx. 70% of ship emissions occur within 400 km of coastlines, and ship emissions further travel in the atmosphere over several hundreds of kilometres [21]. Shipping represents approx. 15% and 13% of global anthropogenic nitrogen oxide (NO$_x$) and SO$_x$ emissions. Particulate matter (PM2.5) emissions from ships vary regionally, representing 7% of the regional total in Africa, 4.4% in Europe, 4.2% in North America, 3.4% in South-East Asia and 22% in Oceania [22].

The IMO controls SO$_x$ and NO$_x$ emissions of ships and regional or global regulations are anticipated for BC (PM and PN indirectly linked) and CH$_4$ emissions. SO$_x$ emissions are decreasing along with the IMO's global fuel sulphur limit of 0.5% in 2020 (or SO$_x$ scrubbers to be used), reduced from 4.5% to 3.5% already in 2012. The IMO has also set regional emission control areas for SO$_x$ (SECA, 0.1% sulphur limit in 2015) and NO$_x$ (NECA, in force from 2021 for new-builds).

Ship emissions to air are products of the complete combustion of fuel (e.g., CO$_2$ and SO$_x$), or oxidation of intake air nitrogen (NO$_x$), while some are products of the incomplete combustion of fuel, such as hydrocarbons (HCs, including CH$_4$), carbon monoxide (CO), formaldehyde, PM and its constituents (BC, polyaromatic hydrocarbons (PAHs)) and particle number (PN) emissions. Some pollutants form in exhaust aftertreatment systems, such as nitrogen dioxide (NO$_2$), ammonia (NH$_3$), and N$_2$O. Heavy metal emissions may originate also from fuel, lubricating oil and engine wear.

SO$_x$ and NO$_x$ emissions affect terrestrial and aquatic ecosystems through acid rain and the eutrophication of waters by nitrogen-containing nutrients. NO$_x$ emissions in the atmosphere form ground-level ozone in combination with organic compounds in the presence of heat and sunlight. Additionally, engine-out NO gradually oxidises in the atmosphere to become NO$_2$, which causes adverse respiratory effects and further reacts to nitric acid (HNO$_3$) and other compounds. The NO$_2$ share in engine-out emissions is low, but increased NO$_2$ formation is known from oxidative aftertreatment devices such as diesel particulate filters (DPFs) and catalysts [23], which must be taken into account if these technologies are adopted in ships. Shipping substantially contributes to overall NO$_x$ emissions, and specifically in harbours leading to high NO$_x$ concentrations in the ambient air near port communities and also in the centers of cities away from the port [24].

Concerning human health, PM, PN and BC emissions are particularly harmful. Particle emissions are linked to heart and pulmonary diseases and recently Alzheimer's disease [25,26]. Particles may carry species, such as PAHs related to carcinogenic and mutagenic activity [27–33]. Reactive compounds and metals potentially cause inflammation and tissue damage [34–36]. Notably, priority PAHs as mobile-source air toxics are defined, including benzo(a)pyrene [37,38]. The residual fuel use in diesel engines emits exhaust particles with marked oxidative activity on the epithelial lining fluid in the lungs [39]. Ship PM2.5 emissions near port communities [40] contribute to a health risk disparity based on ethnicity and income since low-income households are overrepresented in the affected populations near harbours [41].

Other emission species considered for their adverse health and environmental impacts include NH$_3$ and formaldehyde. In the atmosphere, NH$_3$ and ammonium aerosols adversely affect health, vegetation, climate, and visibility. In urban areas, NH$_3$ is an important secondary aerosol source in the presence of PM and NO$_x$ [42]. Formaldehyde is present predominantly indoors, but transport is also a source of increased ambient concentrations from the combustion of fuels and secondary photochemical reactions. Formaldehyde is carcinogenic (IARC Group 1), [33] an irritant to the eyes, skin, and respiratory tract in humans [43] and contributes to the formation of tropospheric ozone [44]. CH$_4$ and N$_2$O are typically not recognized as air pollutants. However, CH$_4$ contributes to the formation of tropospheric ozone in regions where background CH$_4$ dominates [45–47], while the ozone-forming potential of CH$_4$ is low when compared to many other volatile organic compounds present in polluted urban areas [48]. N$_2$O emissions contribute to depleting the stratospheric ozone and its role as an anthropogenic contributor is increasing along with decreasing halo-carbon emissions [49]. CH$_4$ emissions are of concern from LNG use, while N$_2$O emissions are not emitted by marine engines today, but may become relevant emissions due to possibly introduced ammonia as marine fuel since its combustion forms N$_2$O emission. Some exhaust aftertreatment technologies may also induce N$_2$O [50], which needs to be removed.

This review examines possibilities to mitigate ship emissions in the atmosphere, focusing on 1) emissions contributing to global warming, and 2) emissions to air with detrimental impacts on human health and the environment. Marine engines and carbon-neutral fuel options and emission control choices are introduced, and emission factors are presented for large engines at engine loads above 40%. Some of these solutions fit with existing ships and infrastructure, while others require new-builds and are long-term options. Technologies considered to fit in the existing ship fleet (retrofittable) are in focus in this review. Carbon-neutral fuels here refer to a variety of fuels from low-carbon to carbon-negative, balancing the emissions of the fuel pool. These can be non-fossil fuels produced from renewable sources, waste, or hydrogen and captured (circular) CO$_2$, which does not increase the balance of atmospheric CO$_2$ emissions, although CO$_2$ is the main product of the combustion of carbonaceous fuels in oxygen. These principles are often discussed with carbon capture and storage (CCS) or utilization (CCU). The burden of ship emissions could be reduced also by switching to non-carbon or non-fuel energy, shore power at berth, or fuel cells (FCs), batteries, wind, solar, or nuclear power (or hybrid solutions).

The synthesis and discussion part of this paper considers the pros and cons of carbon-neutral, clean fuels and emission reduction technologies to understand possible ways to mitigate the adverse effects of shipping on the climate, health, and the environment simultaneously (Fig. 1). Knowledge of the solutions presented are combined to evaluate possibilities to reduce adverse climate, environment and health impacts of the marine sector effectively and simultaneously in the near future. External costs of emissions for selected technologies are calculated to provide arguments for financial support instruments and investments. This combined view increases the understanding of the effects of the

Fig. 1. A combination of carbon-neutral fuels and emission-reduction technologies is needed for (near-to-) zero-emission shipping.

identified technologies to reduce ship emissions harmful to climate, health and environment, which is a particularly complex combination as reducing one emission may cause an increase of another emission.

The emission factors are given in the figures as the mass per MJ of fuel, while in the text as the mass per kWh. The emissions presented per fuel energy content enable comparisons between sectors, while emissions per engine output energy compensate for possible changes in engine efficiencies. Numerical emission factors are given in supplementary material.

2. Ships fleet and engine sizes

There are over 128,000 IMO registered vessels in the global fleet with engines of many sizes [51]. The main engines are commonly in the size class of 1–10 MW, while the sizes of auxiliary engines are typically around 1 MW (Fig. 2). Engines above 20 MW are mainly slow-speed diesel (SSD) 2-stroke engines, which are typical in large ships such as container ships, bulk carriers, and oil tankers, but their number is low. These SSD engines consume over 70% of marine fuels and they emit a major part of global ship emissions. Medium-speed diesel (MSD) four-stroke engines consume 19% of marine fuels globally, mostly distillates. In the Arctic, smaller fishing and supply vessels may use high-speed diesel (HSD) engines [51], which are not the topic of this review which focuses on MSD and SSD engines.

The fuel type, engine size and load affect emissions from traditional marine engines. The load dependence of emissions from incomplete combustion (e.g., BC in Fig. 3) is of special concern when travelling at low speeds in regions with intense traffic, for instance, while manoeuvring in harbour areas [52–54]. Slow steaming is one option to reduce fuel consumption and CO_2 emissions of ships that otherwise tend to operate at high speeds (e.g., container ships). A reduced speed could be 18–20 knots [55]. However, this may lead to increases in some exhaust emissions, since marine engines are typically optimised for operation at high loads to achieve efficient combustion and to minimise emissions from incomplete combustion. Hence, engines need to be "de-rated" to perform optimally at lower loads. Another option is to maintain the recommended load range by selecting suitable routes, or by adjusting the number of engines running in regions where the speed of ships changes frequently, or by using hybrid systems.

The load dependence of incomplete combustion is less pronounced for modern marine engines than for older engines and so are the overall emissions [60]. The age of the fleet affects the emission level and the load dependence of the emissions. The fleet of large ships is younger (24–28% built within 0–4 years, 16–22% older than 15 years) than the fleet of medium and small ships (only 12–17% are new, while 39% are
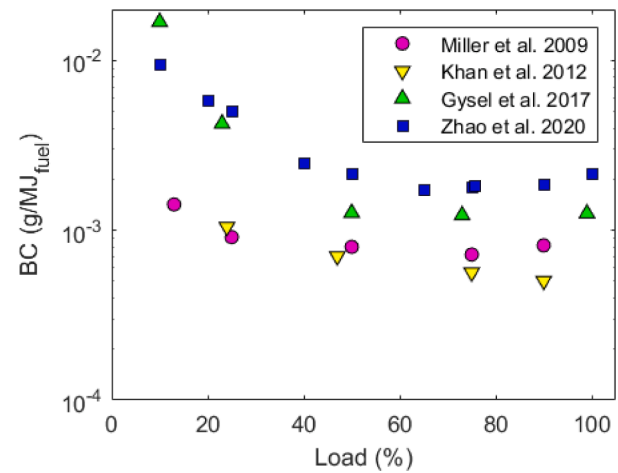

Fig. 3. Relationship between BC emissions and engine load for four marine engines with maximum continuous power of 54.84 MW 94 1/min Miller et al. [56] 68.5 MW, 97 1/min Khan et al. [57] 6.7 MW 512 1/min Gysel et al. [58] and 15.5 MW 88 1/min Zhao et al. [59]. All engines were operating with high sulphur residual fuel except in Gysel et al. [58] with low sulphur (0.009%) residual fuel.

older than 15 years). Approximately 61% of small ships are older than 15 years [61]. The non-optimised use of engines is anticipated to further diminish along with energy efficiency targets, hybridisation [62–64] and controlled operations in harbour regions, such as California's "At-Berth Regulation" [65] and proposed maritime zero-emissions at berth in the EU [6]. Hence the reviewed literature here is limited to engine loads above 40%.

3. Carbon-neutral and low-carbon fuels to reduce climate change impact of shipping

3.1. GHG WtW emissions for fuel alternatives

Fossil marine fuels can be switched to non-fossil counterparts that are chemically similar but produced differently (Table 1). These "drop-in" fuels resemble diesel, LNG or methanol. However, such fuels are not much currently used in shipping: less than 1% of marine fuels today are biofuels and even less meet the stringent criteria such as the Renewable Energy Directive update (RED II).

Fuels carbon-neutrality means that the fuel's WtW net GHG emissions are negligible, viz. carbon is not added to the atmosphere regardless of the carbon content of the fuel. This is the case for example when using biogenic or "circulated, reused, recycled" carbon in fuel production. Not all renewable fuels are carbon-neutral since for some fuels only modest WtW carbon reductions are achieved when compared to fossil fuels. On the other hand, some renewable fuels can even be carbon-negative, if the raw materials would otherwise degrade to CH_4 and CO_2 or if carbonaceous side-products are stored permanently to be removed from the carbon cycle. The WtW GHG emissions include emissions of producing, distributing and consuming fuels. WtW emissions for fuels mainly depend on the upstream emissions of production, for which case-specific and regional aspects need consideration, e.g., the availability of excess heat or the use of by-products. GHG evaluations focusing on marine fuels are still limited, while many studies are available for road transport, one example reports approximately 73 gCO_2eq/MJ for diesel cars using fossil fuel [72,73], which is lower emission than reported for fossil marine HFO in Table 1. Examples of WtW GHG emissions (CO_2eq on GWP100) are given in Table 1 indicating variations depending on the assumptions made.

Regulations on measures to meet the carbon intensity targets of the fuel pool vary. For example, in Europe, stringent GHG criteria for each
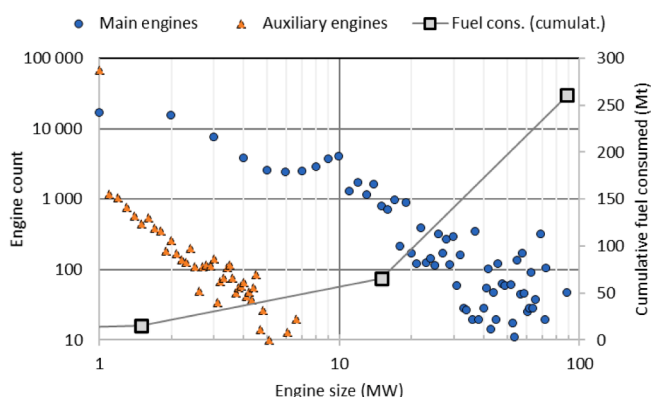

Fig. 2. The number of main and auxiliary engines in different sizes (AIS database accessed by FMI) and the fuel consumed (grey line) annually in SSD, MSD and HDS engines [51] with the distribution in engine size classes. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).

Table 1
Marine fuel options and their renewable or carbon-neutral counterparts.

Engine	Carbon-neutral "drop-in" (fossil as reference)	State	WtW gCO$_2$eq/MJ
Diesel engine	HFO fossil reference	Liquid	99 (**) [a]; 97 [b]; 87 [c]
	Waste oils, fats	Liquid	2 (waste) [d]
	HVO*/FAME*	Liquid	14–17 (used oil) [d], 41 (waste oil) [c]; 23 [e]
	BTL, e-diesel	Liquid	5–20 [d]; 21 (wood residues) [c]
	Pyrolysis oil, upgraded (plastics, cellulosic)	Liquid	5–20 [d]
Gas engines	LNG fossil	Gas	78 [a]; 67 [b]; 79 [c]
	LBG*, biomethane	Gas	12.8–17.2 (ligno-cellulosic) [f]; 24 [a]; 13 (waste) [c]; 51 [d]; −5 (municipal waste) [d]
	e-methane*	Gas	6 [a]
Alcohol engines	Biomethanol/e-methanol	Liquid	5–20 [d]; 18 [c]; 10–40 [g]; −55 (cow manure) [g]; 36–46 (lignocellulosic) [f]
	Ethanol	Liquid	0–25 (lingocellulosic) [d]; 70 (corn) [e]

Hydrogen, batteries, dimethyl ether (DME), ammonia in long-term (Note: electricity EVs 24 gCO$_2$eq/MJ) [e]

* LBG=liquid biogas, biomethane; e-methane is called also synthetic natural gas; BTL=Biomass-to-liquids; GTL=Gas-to-liquids: FAME=fatty acid methyl ester; HVO=Hydrotreated oils and fats.
** HFO 697 MGO 686 g/kWh (2-stroke SSD).
a 2-stroke DF engine [66].
b [67].
c [68].
d [69].
e [70].
f [1].
g [71].

fuel are set in RED II, while in California the balance of the total fuel pool is evaluated by the California Air Resources Board (CARB). RED II in Europe defines minimum GHG emission savings of at least 65% (from 1.1.2021). The FuelEU Maritime Initiative (within the "Fit for 55" package) defines that upstream WtT emissions are determined according to RED II (EU 2018/2001) for biofuels, biogas, renewable fuels of non-biological origin and recycled carbon fuels. A special feature of RED II is the possibility to multiply the energy content of transport fuels from, e.g., waste and cellulosic materials. The factor is 1.2 for compliant fuels supplied in the aviation and maritime sectors. In California, CARB's low carbon fuel standard (LCFS) defines the WtW carbon intensity for fuels and the market determines the fuel mix to meet the targets [70]. CARB has also an "at berth" regulation recommending switching engine power to grid electricity at berth or using only LSFS fuels at berth [65]. These regulations verify that substantial GHG emission reductions can be achieved with compliant fuels.

The potential for GHG emissions reduction by switching from HFO to fossil LNG is up to 30% compared to diesel fuel as LNG has a lower carbon-to-hydrogen ratio. However, the GHG benefit obtained with LNG may be lost to some extent by the slip of unburned methane, a strong GHG gas. For LNG, a 21% GHG reduction compared with HFO use has been reported and a 6–23% reduction depending on e.g. methane slip [66,74]. Winebrake et al. [75] reported on a WtW analysis indicating that NG-based marine transportation in the US can provide significant local environmental benefits, but renewable fuel is needed to avoid a global warming penalty. The IEA [76] evaluated only a 10% GHG abatement potential when shifting 50% of the international shipping fleet to LNG, and less if the methane slip is accounted for (see "Methane emissions" section).

The carbon footprint of e-fuels depends on the electricity used in the production of hydrogen: a prerequisite for low GHG emissions for

hydrogen is carbon-free electricity in the production instead of fossil methane reforming which is used today. For electricity with relatively high carbon emissions of 375 gCO$_2$e/kWh, WtW emissions for e-methane, e-methanol and e-diesel are also high (176–190 gCO$_2$eq/MJ), while for example with wind electricity of 7–56 gCO$_2$eq/kWh, respective WtW emissions are low (2.5–30.5 gCO$_2$eq/MJ) [1]. Decarbonising the power sector is progressing globally, and low-carbon electricity is already available in some regions. The IEA [76] estimates that the global emissions of electricity production must decrease below 100 gCO2/kWh by 2040 to achieve the two-degree target. In some regions, CO$_2$eq emissions of electricity production are already relatively low (e.g. on average 129 gCO$_2$eq/kWh in 2017 in Finland). According to Koponen and Hannula [77] when the carbon intensity of electricity remains under 84–110 gCO$_2$/kWh, 70% emission savings compared to fossil fuels can be achieved with e-fuels. The carbon emissions for NH$_3$ and hydrogen fuels depend on the origin of electricity used in their production, similarly as for the e-fuels. Hydrogen production can be classified according to the production process applied to grey (fossil methane reforming), blue (fossil methane reforming with CCS), turquoise (methane pyrolysis) and green (electrolysis using renewable electricity), however, even for the green hydrogen, a considerable adverse climate impact may arise from e.g. the electricity supply. In the analysis by Hermesmann and Müller [78], the best-case scenario for green hydrogen production based on offshore wind electricity resulted in a climate warming impact of 4.9 gCO$_2$/MJ, while the estimate for grey hydrogen was 81 gCO$_2$/MJ. For blue hydrogen, climate warming impact was estimated as only approximately 3.4% lower than that for grey hydrogen.

With fossil fuels, the technology to reduce GHG emissions would be carbon capture on-board the ship, and a demonstration of this concept is announced, e.g., by Wärtsilä and Solvang [79]. Captured carbon could be then stored (CCS) or utilised (CCU). One of the concepts suggested by the HyMethShip project is based on carbon capture of electro-methanol reformation on-board pre-combustion of hydrogen. The project aims to improve the efficiency of the process, while also achieving a reduction of up to 97% of CO$_2$, over 80% of NO$_x$ emissions and elimination of SO$_x$ and PM emissions [80,81]. Generally, carbon capture from sustainable fuels on-board the ship could enable a very low, even negative, carbon balance.

3.2. Suitability of fuel alternatives for different engine technologies

3.2.1. Carbon-neutral and low-carbon fuels for diesel engines

Marine fuels today are fossil fuels. In 2018, the share of heavy fuel oils was 66%, distillate fuels 31%, LNG 3% and less than 1% of methanol and biofuels [7,82]. Hence, replacing these fuels with diesel-type carbon-neutral alternative fuels is relatively straightforward for use in diesel engines.

The total consumption of marine fuels was 266.3 Mt globally in 2015, which is approx. 10% of the total transport fuels (see Supplementary Table S9). Production of biofuels for the transport sector is limited. The global production of FAME biodiesel was 23.5 million tonnes of oil equivalent (Mtoe) in 2015 and that of hydrotreated paraffinic HVO was 4.7 Mtoe with an announced capacity of 11.4 Mtoe for 2022 [83,84]. In road transport, the largest biofuel production volume is for bioethanol (50.1 Mtoe in 2015). In Iceland, the production of e-methanol is approx. 5 kt annually [85]. These limited production volumes illustrate the challenge of replacing fossil marine fuels substantially with their carbon-neutral or low-carbon counterparts.

Until 2020, about 42% of marine fuels was residual fuel oil containing a range of harmful substances, such as sulphur, heavy metals (e.g., V and Ni in ash), catalyst particles ("fines") from the refining process (Al, Si), asphaltenes and PAHs. In 2020, the IMO regulation reduced the global fuel sulphur content limit from 3.5 to 0.5% with an impact on the demand for low-sulfur marine fuels (and prices). Additionally, blending residual fuel components with distillate fuels became common based on viscosities higher than 20 mm^2/s for more than 90% of very low sulfur

fuel oil (VLSFO) on the market [86]. *Marine distillate fuels below 0.1% sulfur* content used in SECAs and EU port areas are still high-sulfur fuels when compared to road diesel fuels with a sulphur limit of 0.001%. International standard ISO 8217 specifies properties of residual marine (RM) fuels (the third letter indicating grade, e.g., RMA and RMB classified by their viscosities) and distillate marine (DM) fuels. For instance, the DMA class (marine gas oil, MGO) is free from residual fuel, and DMB class (marine diesel oil, MDO) may contain traces of residual fuel. Selected marine fuel properties are presented in supplementary Tables S10-S12.

In large marine diesel engines, oils and fats could be used with minor treatments, such as de-gumming and de-acidifying, while esterification to FAME would be unnecessary. Using oils and fats avoids glycerol by-products of transesterification. Some shipping companies already use biofuels from waste streams, for example, VG Ecofuel [87]. Other raw materials for oils and fats, such as algal and seaweed, could also become feasible for producing fuels [88–90]. For vehicles and non-road HSD diesel engines, oils and fats are transesterified with methanol to produce FAME to improve the fuel properties. ISO 8217 limits the use of FAME up to 7 vol% for use in special grades (DFA, DFZ and DFB) and only "de minimis" 0.5 vol% of FAME is accepted in the regular marine fuel grades (e.g., residual fuels, DMA and DMB).

Another option is to produce HVO from oils and fats by hydrogenation. HVO consists of paraffins (alkanes) and has a very high cetane number and high quality sufficient for road transport [91]. Similar paraffinic fuels can be produced also by the gasification of biomass followed by Fischer-Tropsch (FT) liquefaction to produce BTL fuel. E-diesel is also paraffinic (resembling HVO) and it can be produced from the synthesis of hydrogen and CO_2 using FT liquefaction. The FT process produces hydrocarbons at various chain lengths with fractions suitable for use as jet fuels, diesel or marine fuels with the exact product defined by post-processing of the synthesized hydrocarbons [92,93].

Bio-oils produced by the pyrolysis of bio-waste or cellulosic feedstocks are challenging for internal combustion engines (ICEs), even if the bio-oil is upgraded. Bio-oils based on tyres are less challenging than those based on cellulosic raw materials. Bio-oils may contain oxygen and acids, and their properties vary depending on the feedstock, production process, and degree of upgrading. The corrosiveness of bio-oils is one of the concerns [94–97]. GoodFuels and BTG Biomass Technology Group BV in the Netherlands have announced of building a plant for producing upgraded pyrolysis fuel for shipping to utilise residues and wastes [98]. Good quality bio-oils have been reported for the pyrolysis of some recycled feedstocks, such as plastics or tyres [99]. For example, polyethene (PE) and PET are feasible feedstocks [100], while special concern regards the chlorine content of fuel when the material contains e.g. polyvinyl chloride (PVC). Hossain et al. [101] reported of tyre oil having the most fuel properties similar to diesel fuel (e.g. energy content, viscosity, density), while the sulphur content was substantial (3500 mg/km). Teoh et al. [99] found also many properties of tyre oil resembling those of diesel fuel, however, the flash point was low (below 40 °C), carbon residue and acid number were high (1.07 wt% and 1.03 gKOH/g, respectively). Using renewable diesel-type fuels in marine diesel engines and fuel infrastructure is in principle straightforward, however, challenges with storage, blending and end-use may occur. For example, blends of distillate-type diesel components (e.g., FAME, paraffins) with residual marine fuels may cause the separation of asphaltenes from residual fuel and the formation of sludge, filter clogging and engine damage. Generally, the same types of components fit best with each other, hence, paraffinic components and FAME with marine distillates. Pyrolysis oils are the most challenging components since experience in their use as marine fuels is almost non-existent. Compatibility testing for marine fuel blends is a common procedure, but traditional methods may not apply to new components. The compatibility problems of diesel-type renewable fuels can be tackled by modified fuel handling in the ships, as well as by making engine adjustments, retrofitting injectors and engine optimization or by fuel processing and upgrading technologies.

3.2.2. Carbon-neutral and low-carbon fuels for gas engines (LNG-type fuels)

LNG, consisting mainly of methane, is the major alternative marine fuel on the market today, however, from fossil origin. Its share was about 2.4% of global marine fuel consumption in 2015 [51]. Overall, natural gas (NG) is one of the major energy sources and represented 22.2% of the world's total primary energy supply in 2017, and 3.7% (104.7 Mtoe) of energy consumed in the transport sector [102], hence its availability is considerable. For shipping, methane is liquefied to produce LNG by cooling it to −162 °C to increase its energy density and for easier storage and transport, while for vehicles natural gas is mainly used in compressed form (CNG). LNG use in shipping has been favoured due to its availability and tolerable price when compared with conventional marine fuels (Acciaro, 2014 in [103]). An important aspect favouring LNG use has been also its low SO_x and potentially low NO_x emissions. In 2019, the number of LNG-powered ships was 756, of which 539 were LNG carriers [104].

Carbon-neutral methane can be produced using several pathways: a) LBG from biogas by cleaning and upgrading (removal of CO_2 and impurities); b) LBG from biomass through gasification and methanation; c) e-methane from renewable hydrogen and CO_2 by synthesis (the Sabatier process) [105]. The methane streams from different pathways are sufficiently similar to fossil LNG to be compatible with respective engines.

Hythane is a fuel option achieved by mixing compressed NG with hydrogen [106–109]. Hythane as a liquid fuel-mix in a tank is not an option due to the different liquefaction temperatures of methane (−162 °C) and hydrogen (−253 °C). However, solutions for the injection of hydrogen for addition in LNG DF engines could be developed.

For using methane (LNG or carbon-neutral methane) as a marine fuel, there are three marine gas engine types today: low-pressure spark ignited engines, low-pressure dual fuel (LPDF), and high-pressure dual fuel (HPDF) engines. LPDF is the most popular LNG engine technology with at least 350 ships (e.g., LNG carriers, car/passenger ferries, cruise ships), while HPDF is used for large low-speed oceangoing vessels in less than 100 ships [104]. The high octane number of methane makes it compatible with spark-ignition engines and it is used as a fuel in marine engines with the lean burn spark ignition (LBSI) technology. DF engines use a pilot injection of distillate fuel to ignite an NG and air mixture. In this concept, distillate fuel can be used as the back-up fuel, which is an advantage due to limited LNG infrastructure [110]. The efficiency of both compression ignition and LBSI marine gas engines can be high (e.g., the fuel consumption of 166–181 g/kWh, 7154–7804 kJ/kWh for a Wärtsilä 31SG gas engine). However, the required safety measures and large space of LNG tanks on board ships are demanding when compared to diesel. Even so, investments in ships and harbour infrastructure for LNG use are expanding (Acciaro, 2014 in [103]).

Carbon-neutral and low-carbon methanol and ethanol fuels are compatible with alcohol engines. Methanol is a liquid fuel, currently produced from fossil natural gas or to a lesser extent from renewable raw materials. In practice, methanol is another option to liquefy methane besides LNG.

Carbon-neutral methanol can be produced from carbon-neutral methane, i.e.: a) biomethanol from cellulosic biomass or waste; or b) e-methanol from e-methane or by direct hydrogenation of CO_2. George Olah has suggested that the methanol economy would offer means to realise a circular energy concept [111]. *Ethanol* is anticipated to remain for use in road transport [83]. Methanol fuel produced by thermochemical and electro-fuel platforms would be more economical than producing ethanol with these processes. This aspect combined with the existing infrastructure and marine methanol engines makes it an interesting fuel for the shipping sector.

Methanol is used as marine fuel in the Stena Germanica car ferry in Sweden using Wärtsilä's methanol DF retrofit concept (Sulzer ZA40S

engines) and on more than ten ocean-going tankers with MAN's new-build methanol DF engines (ME-LGI) [112]. In a dual-fuel engine, a pilot fuel ignites the methanol (5% diesel and 95% methanol). MAN's methanol DF concept for 2-stroke SSD engines and Wärtsilä's concept for 4-stroke MSD engines are feasible for retrofitting and new-builds. In these concepts, methanol is injected under high pressure into the cylinder chamber. One injector for diesel and the other for methanol are used in the MAN concept [113], while a single injector is used to inject diesel and methanol in the Wärtsilä concept [114]. A so called 'fumigation' concept is also considered for methanol DF engines based on injection at low pressure in the inlet manifold [112]. Methanol tanks can be at the bottom of the ship, which is an easier solution than restricted placing options for LNG or diesel tanks [90]. For smaller vessels, additised methanol could be used in alcohol diesel engine. In the Scania ethanol engine concept, which has been used in buses since 1985 [115, 116], an ignition improver and lubricity additives to methanol enable its use in a diesel engine with an increased compression ratio and a special fuel injection system [117]. For using marine methanol, safety measures and minor modifications to the harbour infrastructure are needed.

For other marine fuels, special engines can use carried chemicals as fuels, for example, LPG-powered DF engines on very large gas carriers [118,119].

3.2.3. Other carbon-neutral and low-carbon options (DME, ammonia, hydrogen, fuel cells, batteries, wind, solar, nuclear)

Dimethyl ether (DME) has been demonstrated in some special applications, however, engines for their use are not on the market for the maritime sector. DME is manufactured from fossil, carbon-neutral or low-carbon methanol, which is a marine fuel itself. DME is a gaseous fuel needing modest pressure for liquefaction (similarly to LPG). Diesel engines need relatively mild modifications to use DME [120,121].

NH_3 can be used in FCs or modified ICEs, and it is considered as a marine fuel [50,122,123]. NH_3 is carbon-free fuel produced from hydrogen and nitrogen (from the air) with the Haber-Bosch process. However, the WtW carbon-balance of NH_3 depends on the origin of electricity used for its production similarly to e-fuels (Section 3.1). Safety concerns are related to NH_3 fuel, and thus it is converted to urea for use as a reducing agent in the NO_x reduction catalyst, SCR. NH_3 is an invisible, toxic gas and the limit for long-term exposure is 25–30 ppm (NIOSH limit), 300 ppm is immediately dangerous, and 5000 ppm is fatal within minutes. NH_3 is corrosive and can cause permanent injuries (eyes, alkali burns etc.) [124]. The combustion of NH_3 produces N_2O [50] which has a high GWP100 of 265 [11]. When considering NH_3 as fuel for ICE, exhaust emission control to remove N_2O is essential.

Hydrogen gas could be used in ICEs or FCs as such, however, as the lightest gaseous molecule, its storage and distribution are challenging in compressed or liquefied form. A relatively new concept is a reversible system of liquid organic hydrogen carriers (LOHC) [125,126]. The LOHC concept is still not proven, and the temperature needed for hydrogen release is high. Solid-state hydrogen storage carriers may have sufficient hydrogen storage capacities, but the weight of the system is high and hydrogen release is challenging. So far, these hydrogen storage options don't have sufficient energy density, non-toxicity or usability for the main engines of large ships. For easier storage and transport, hydrogen can be converted irreversibly to e-fuels (e-diesel, e-methane, e-methanol, e-ammonia, formic acid) or stored in reversible liquid or solid-state systems [126]. The usability of formic acid and the purity of the released hydrogen is challenging for FCs. While compressed hydrogen requires the least amount of energy, the energy-consuming e-diesel fuel has the highest energy-density and fits the present infrastructure. From all hydrogen storage options, bunkering infrastructure for large ships is widely available only for diesel-type fuels and to some extent for LNG and methanol.

Fuel cells can utilise hydrogen, methane, methanol and ammonia with high efficiency. FCs using hydrogen and methanol have been demonstrated in shipping [127]. FCs have high efficiencies, e.g.,

50–60% for proton exchange membrane fuel cells (PEMFC) and 60% for solid oxide fuel cells (SOFCs), and even up to 85% with heat recovery. However, FCs are space demanding, thus considered currently for auxiliary engines, hybrid and low-power machinery, with an estimated 2–20% CO_2 reduction potential [90]. PEMFC technology is sensitive to impurities, while SOFCs can pose a safety concern because of the high operating temperatures (800–1000 °C).

All-electric ships' emissions depend on upstream emissions and thus mainly on emissions for electricity generation. Batteries are already installed on ships for short-distance routes. The costs of batteries are foreseen to decrease, e.g., lithium-ion battery pack prices are expected to be as low as $73 per kWh by 2030 (Bloomberg in [90]). Batteries are heavy, hence all-electric oceangoing ships are foreseen to be implausible, although they can be adapted for shorter routes [128,129]. Hybridisation is probably also an option for smaller vessels to achieve fuel savings [130,131]. California started At-Berth Regulation in 2014 for three vessel categories at six California ports to reduce PM and NO_x emissions from ocean-going vessels' auxiliary engines while they are docked at California ports [65]. An update At-Berth Regulation will be effective in 2023 for which vessels are required to use shore power or fuels that will emit equal or less than shore power (emissions from electric power generation) while docked to meet carbon neutrality [132].

Wind, solar, and nuclear power are options as energy sources for shipping, however, wind and solar are not to replace the main engines of large ships at their current stage of development. Kites and rotors are mature but most effective only at slow speeds (e.g., kites below 16 knots). Rotors are challenging for container ships due to interference with cargo handling, but they do achieve fuel savings. Flettner rotors are used on ships [133]. Solar and wind technology is suggested for auxiliary power demands [90]. Nuclear propulsion for military and submarine purposes has been used since 1955 and is used, e.g., for icebreakers. Approx. 200 reactors in Russia enable running for long periods without refuelling. However, it is unlikely that many countries would allow nuclear vessels to enter their ports due to safety risks. The environmental consequences of a possible accident would be worse for nuclear ships along inhabited coastlines than in power plants. Radioactive fuel and its storage needs, training of staff, nuclear regulations etc. are also of concern. In 2017, China decided to invest in the development of two prototype molten salt nuclear reactors for aircraft carriers, drones, and military aircraft [90].

4. Exhaust emission reduction

Upstream emissions of fuel production are decisive for WtW CO_2 emissions, however, the downstream emissions of CH_4, N_2O and BC also have a significant impact. Exhaust emissions harmful to health and the environment are NO_x, SO_x, NH_3, formaldehyde, particles (PM, PN, BC) and related PAHs and heavy metals. Secondary reactions of emissions in the atmosphere may further contribute to tropospheric ozone formation, deplete stratospheric ozone, or form secondary aerosols (Table 2). Fuel, engine and aftertreatment technologies can remove these harmful species of exhaust substantially. One special feature of carbon-neutral fuels is their sulphur-free nature enabling the utilisation of the most effective exhaust aftertreatment technologies. Exhaust aftertreatment technologies for reducing harmful pollutants may increase fuel consumption (typically up to 10%) and solutions are needed to balance this also, e.g., waste heat recovery systems [134].

The IMO regulates SO_x and NO_x emissions (MARPOL Annex VI) as described in the Background section and ship emission control systems were first developed to tackle these emissions. The IMO limits SO_x emissions by setting the maximum sulphur content limit for marine fuels or using high-sulphur fuels in combination with SO_x scrubbers. The IMO limits fuel sulphur content globally (0.5% in 2020 or SO_x scrubbers to be used, from 4.5% to 3.5% in 2012) and in SECAs to 0.1% in 2015 (earlier from 1.5% to 1%) [135]. The IMO is anticipated to limit also BC

Table 2

Classification of the effect of emission species on climate, health, environment and their contribution through secondary reactions (see the Background section).

Emission	Climate	Health	Environment	Reactions
CO_2	Yes			
SO_x	Indirect	Yes	Yes	c
NO_x, NO_2		Yes	Yes	a, c
Methane	Yes	Indirect	Indirect	a
Formaldehyde		Yes	Indirect	a
N_2O	Yes	Indirect		b
NH_3		Yes	Yes	c
Particles	Yes*	Yes		
BC	Yes	Yes	Indirect	
PAH		Yes	Yes	
Heavy metals		Yes	Yes	

[a] Forming ground-level ozone.
[b] Depleting stratospheric ozone.
[c] Forming secondary aerosols.
[*] Via constituents of PM.

emissions from marine engines, regionally or globally. Regional regulations are set for PM, PN, and methane emissions. The emission standards in the EU for inland waterways, EU Stage V, are currently the tightest regulations of their kind. Still, on-road regulations are even tighter, for example, "Euro VI" emission standards for heavy-duty vehicles (Table 3) [135]. In this section, ship emissions are presented for different engine, fuel and exhaust aftertreatment technologies (details in supplementary Tables S1-S6).

4.1. SO_x emissions

In the combustion process, sulfur present in fuel (and lubricating oil) forms SO_2, which further converts to SO_3 and the exhaust PM sulphates (see Section 4.5). These contribute also to the atmospheric reactions to ambient sulphate levels. Sulphates cool the climate by reflecting away the sunlight, and hence, reduced SO_2 emissions from shipping are anticipated to increase climate warming. However, simultaneously lower PM emissions reduce the health exposure of shipping [16].

SO_x emissions from marine engines can be reduced by: a) using low-sulphur and sulphur-free fuels (distillates, LNG, methanol, carbon-neutral fuels), and b) using SO_x scrubbers. Since SO_x emissions form by the combustion from sulphur present in the fuel and lubricating oil, SO_x reduction is also achieved by reducing fuel sulphur content. Fuel with 3.5% sulphur content leads theoretically to SO_2 emissions of 14 g/kWh, and fuel with 0.5% sulphur content to SO_2 emissions of 2 g/kWh, respectively. Distillate fuels targeted for SECA regions with a sulphur content below 0.1% result in SO_2 emissions below 0.4 g/kWh (Fig. 4 and supplementary Fig. S2). For high-sulphur residual fuels and low-sulphur distillate fuels, several measurement campaigns have confirmed the relationship between SO_2 emissions and the fuel sulphur content [57,87, 136,137].
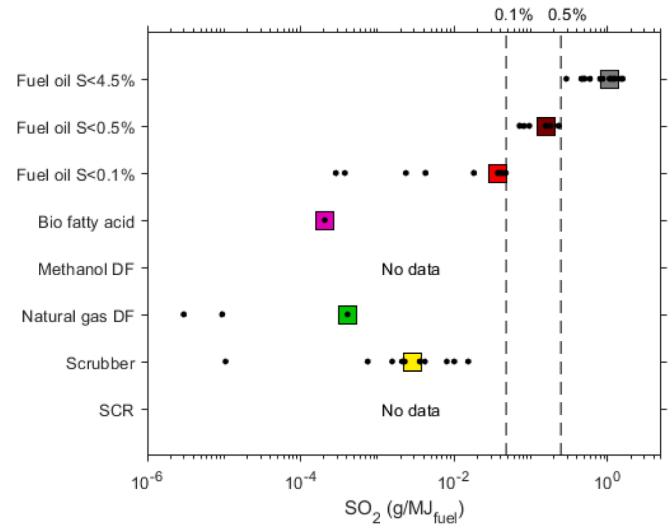
Table 3

Examples of emission standards.

	CO g/kWh	HC	NO_x	PM	PN
EU Stage V 2020 (75–3700 kW)	3.5	0.19	1.8	0.015	1×10^{12}
Euro VI heavy-duty	1.5	0.13	0.4	0.010	8.1×10^{11}
MARPOL Annex VI example.[a, b]			2.26 (1000 1/min)		

[a] Tier III NO_x emissions in NECAs, 3.4 g/kWh (n<130 rpm); $9 \times n^{(-0.2)}$ g/kWh (130 rpm $\leq n <$ 2000 rpm), 2.0 g/kWh ($n \geq$ 2000 rpm).
[b] SO_x emissions from shipping are limited by the IMO's regulation on sulfur content of fuel.

Fig. 4. SO_x emissions from MSD and SSD marine engines using different fuels and exhaust gas treatment technologies. For the fuels, the data is calculated as the SO_2 emissions from the reported fuel sulfur values and for the scrubbers from the measured SO_2 emissions. The small markers indicate individual data points and the large coloured markers represent the median value. Grey: $S <$ 4.5% fuel. Dark red: $S < 0.5$% fuel. Red: $S < 0.1$% fuel. Magenta: fuel with 30% fatty acids. Green: NG with pilot oil ignition. Yellow: scrubber. Methanol DF and SCR are excluded from the Figure since sulfur data was not available for Methanol DF and SCR technology does not affect SO_x emissions. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Sulphur-free carbon-neutral diesel-type fuels containing only minor amounts of sulphur lead to extremely low SO_x emissions, and LNG and methanol are also sulphur-free fuels. The minor amount of SO_x emissions detected when using these fuels originates from the lubricating oil or pilot diesel-type fuel in the DF engine.

SO_x scrubbers enable low SO_x emissions even with high-sulphur residual fuels. Different types of SO_x scrubbers include fresh water (closed loop), seawater (open loop), and hybrid scrubbers (applicable to fresh and seawater), as well as dry scrubbers. Scrubbers were well-known in power plants before they were introduced in ship applications [138]. Scrubbers on-board have demonstrated the potential of SO_2 emissions at a very low level, for example, 0.07 g/kWh using fuel with a sulfur content of 1.9 wt% [139] and generally lower SO_x emissions than when using fuel of 0.1wt% sulphur content. SO_2 emissions of 0.12 g/kWh equal a fuel sulphur content of <0.03wt% (see supplementary Fig. S2). Winnes et al. [140] reported a study on-board a RoPax ferry, on a 9.6 MW common rail engine and a scrubber system using seawater resulted in SO_2 emissions significantly lower when using HFO and a scrubber than when using below 0.1% sulphur fuel oil. Many studies report similar findings for several types of ships and scrubbers, such as a modern cruise ship with a hybrid SO_x scrubber using fuel having 0.65% sulphur content; a RoRo passenger (RoPax) ship equipped with an open loop SO_x scrubber and a diesel oxidation catalyst (DOC) using residual fuel having 1.9% sulphur content [60,136,139,141]; a container ship (1987) retrofitted with a SO_x scrubber with an "open loop" mode at sea and "closed loop" mode in port (fresh water/sodium hydroxide solution) [142]; a RoRo ship and a SO_x scrubber system in an open mode [143] and a scrubber-equipped container ship, a cruise ship and a Ro-Ro ship [144]. Scrubbers can be adjusted for lower SO_2 reduction to save energy, e.g. when operating in non-SECA waters. However, the target values for each of the tested scrubbers are not reported.

Although SO_2 emissions can be reduced by scrubbers by 99%, sulphuric acid (H_2SO_4) can be reduced to a lesser extent [140]. Sulphuric acid, sulphates, PAHs and heavy metals are discussed later with the PM emissions (Section 4.5).

4.2. NO$_x$ emissions (including NO$_2$)

4.2.1. Formation of NO$_x$ in engine

NO$_x$ emissions form in diesel combustion in the reaction of nitrogen and oxygen and the intake air at high temperatures. The nitrogen content of marine fuels (other than ammonia as fuel) is too low for substantial NO$_x$ formation.

Typical engine-out NO$_x$ emissions are approx. 10–20 g/kWh with distillate-type fuels at engine loads higher than 50% MCR (Maximum continuous rating). NO$_x$ emission consists mainly of NO and a minor amount of NO$_2$. NO$_x$ emissions from diesel engines can be reduced by: a) on-engine design and exhaust gas recirculation (EGR); b) emission control systems (e.g. SCR); or c) LNG fuels (or other fuels) leading to low NO$_x$ emissions; and e) to some extent with scrubbers. Reduction of NO$_x$ emissions in SO$_x$ scrubbers is marginal, reportedly 5–10% due to the NO$_2$ transfer into water [60,140]. Furthermore, this reduction is limited to a maximum of 12% to allow the washwater treatment system to prevent the discharge of nitrates (Resolution MEPC.259(68)).

Engine out NO$_x$ control is possible for example by adjustments of the engine parameters, e.g., delayed injection timing, cooling the charge air or using variable valve timing and water injection to the engine. In the aforementioned cases, the lower combustion pressure leads to a lower peak combustion temperature and thus lower NO$_x$ emissions, however, this comes at cost of penalty in fuel economy and increased BC emissions [145,146]. This physical phenomenon is known as the NO$_x$/PM trade-off, or rather the NO$_x$/BC trade-off since other constituents of PM (e.g., organics, sulphates, metals) do not necessarily follow this principle. In the IMO regulations, the NO$_x$ emissions limit increases along with the engine size, allowing larger engines to be tuned towards higher NO$_x$ and lower BC emissions (Fig. 5). For example, higher compression ratios and combustion temperatures increase NO$_x$ emissions while favouring soot oxidation. Additionally, the low speed of larger engines gives more time for soot to be oxidized in the cylinder. The engine technologies to reduce NO$_x$ and PM simultaneously, viz. to disengage the relationship of these emission species, include for example turbochargers and electronic engine control. Fuel efficiency can be improved by engine tuning to high NO$_x$ emissions combined with a NO$_x$ reduction technology, e.g., EGR or SCR, and this combination enables simultaneous abatement of NO$_x$ and PM emissions. EGR is an internal technology of an engine to reduce NO$_x$ emissions by mixing a part of the exhaust gas into the intake combustion air to reduce the oxygen availability and increase the water and CO$_2$ concentration in the intake air, which suppresses combustion temperatures and hence, NO$_x$ formation. On the other hand, EGR tends to increase PM emissions [147] and worsens fuel economy. NO$_x$ emission reduction is traditionally modest with engine internal methods, while new combustion processes could be more efficient [148].

4.2.2. Exhaust aftertreatment to reduce NO$_x$ emissions

An SCR-system utilizes a catalyst and ammonia to reduce NO$_x$ emissions. This procedure with higher engine-out NO$_x$ emissions and aftertreatment allows better fuel economy. In the SCR, the dominant reaction involves NO, NH$_3$, and oxygen reacting to nitrogen and water. Due to toxicity and handling problems associated with NH$_3$, a water solution of urea is typically used and its effective decomposition to ammonia is needed upstream of the SCR catalyst. Optimization of the urea feed is important to avoid NH$_3$ slip downstream of the catalyst. SCR catalysts in ship applications are typically vanadium (V$_2$O$_5$) catalysts with high activity and sulphur tolerance [149–151]. SCR technology is compatible even with residual marine fuels since monolithic fixed beds have square holes, which are large enough to avoid clogging and poisoning [103,147]. Significant NO$_x$ reductions of nearly 90% are reported for ships using SCR as indicated also in Fig. 6a. NO$_x$ reductions of 90–91% were reported for SCR retrofit of auxiliary engines on the ocean-going vessel using HFO at loads of 35%, 50% and 67%, at exhaust temperature of 327–363 °C [152]. NO$_x$ reductions above 90% have been achieved for a ship operating at cruise speed at a 75% load [153]. For

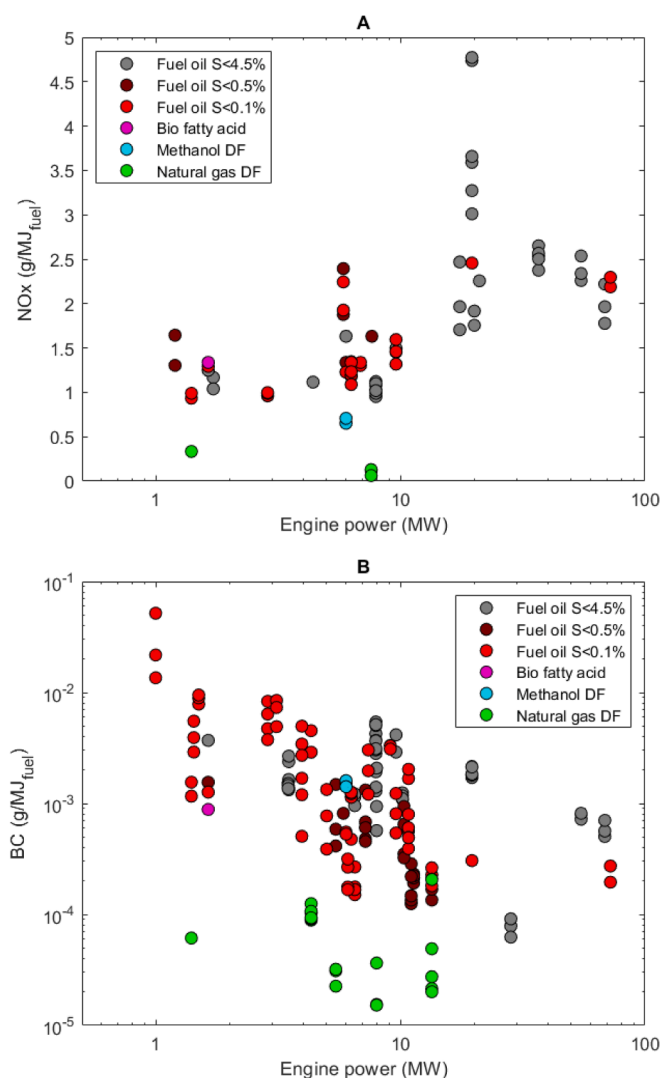**Fig. 5.** a) NOx and b) BC emissions as a function of max engine power (MW) from marine engines at different engine sizes. Only data points with loads greater than 40% of the MCR are shown in the figure to limit the effect of the engine load on emissions. References are shown in the Supplementary material. In legend, $S < 4.5\%$ means $S = 0.5$–4.5% and for lower sulphur contents respective ranges.

two ferry engines fitted with SCR, the NO$_x$ conversions were found to be between 36% and 94% depending on the catalyst temperature [154]. An SCR provides greater NO$_x$ reduction when the exhaust temperature is within an appropriate range. With vanadium-based SCR systems and an HFO fuel, NO$_x$ reduction efficiencies have been found to vary from 75% to 99% at 340 °C [155]. In continuation work, the NO$_x$ reduction efficiency reached nearly 90% efficiency at 340–400 °C, but only 70% at 260 °C [149]. By increasing the catalyst loading, the NO$_x$ removal efficiency increased at lower temperatures without significant changes at higher temperatures. The catalyst chemistry could also be modified for this purpose. A combination of the SCR and DPF yielding ultra-low emissions has also been studied for medium-speed engines [156].

4.2.3. The effect of fuels on the NO$_x$ emissions

Fuels also affect NO$_x$ emissions depending on the combination of fuel and engine technology used. Theoretical flame temperatures of chemical compounds at similar chain lengths and boiling points are the highest for aromatics followed by olefins, and the lowest for paraffins, alcohols and ethers [157]. However, this applies in adiabatic and stoichiometric conditions, while combustion under pressure in the cylinder of an
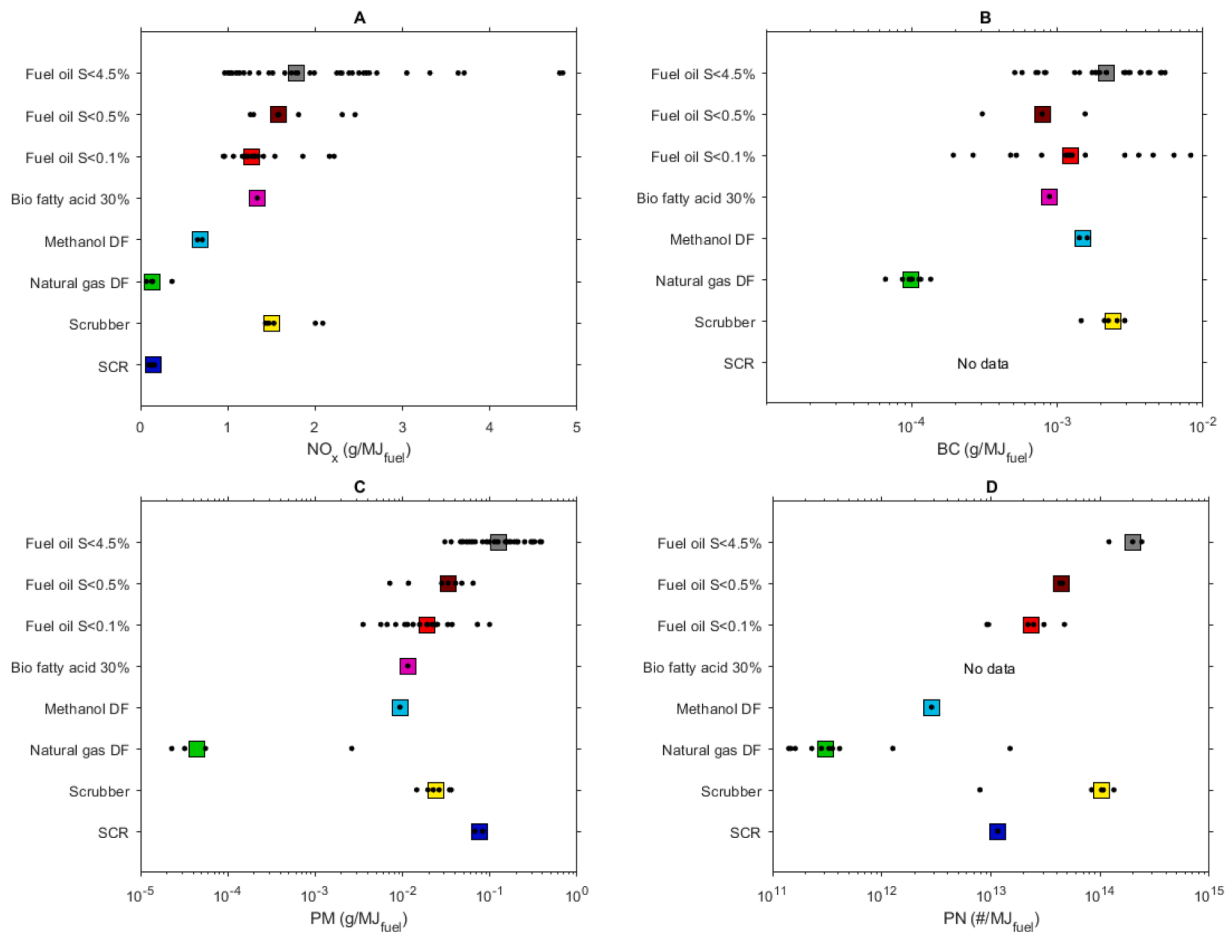
Fig. 6. Emissions from marine engines using different fuels and exhaust gas treatment technologies. MSD and SSD engines, engine loads equal or above 40% MCR: a) NO_x emissions. b) BC emissions. c) PM emissions. d) PNnv emissions (non-volatile). Small markers represent individual data points and large coloured markers represent the median values. Grey: S <4.5% fuel. Dark red: S < 0.5% fuel. Red: S< 0.1% fuel. Magenta: diesel fuel with 30% fatty acids. Cyan: methanol with pilot oil ignition. Green natural gas with pilot oil ignition. Yellow: scrubber. Blue: SCR. Note: Methanol DF BC result is from one retrofit concept and may be different for other engine or combustion principles. Numerical values are presented in the Supplementary material (Appendix S1). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

internal combustion engine is complex. Particularly, if air-to-fuel ratio is not adjusted corresponding to the amount of oxygen bound in fuel, the mixture may become leaner and the combustion temperature higher leading to elevated NO_x emissions.

For LNG, NO_x emissions can be reduced along with lower peak temperatures in the cylinder during combustion [158]. LNG engines tuned to low NO_x may achieve Tier III NOx levels even without SCR (primarily LPDF and spark ignition ones), while other LNG engines need SCR to reach similar NO_x emission levels (primarily HPDF ones) [104]. In on-board measurements, LNG DF marine engines have shown NO_x emissions on average of approx. 1.2 g/kWh [159]. NG combustion in lean-burn conditions tends to increase the NO_2/NO_x ratio [158,160, 161].

Limited data for methanol DF engines indicate lower NO_x emissions than those for marine diesel engines using residual or distillate fuels, although higher than that for LNG DF or SCR-equipped marine diesel engines [114]. A special HSD diesel engine (Scania EEV Ethanol DC9 270 hp) using methanol additised with an ignition improver has shown NO_x emissions of 2.2 g/kWh [162].

Paraffinic fuels (HVO, GTL, XTL) for diesel engines generally reduce NO_x emissions due to the lower combustion temperature of saturated compounds (alkanes) in the absence of unsaturated bonds (aromatics and olefins). These fuels also have high cetane numbers and hydrogen-to-carbon ratios. Additionally, low densities and viscosities of paraffinic fuels may retard dynamic injection timing and hence enhance the

reduction of NO_x emissions [91,163–166]. Low NO_x emissions for paraffinic fuels have been reported for road and non-road applications, while only a few studies are available on using paraffinic fuels in marine applications. In comparison with marine gas oil, the reduction in NO_x emissions with paraffinic HVO has been 10–19% [167,168]. NO_x reduction was significant (13%) also in the 2-stroke, small bore, high-speed engine [169].

FAME biodiesels are often reported to slightly increase the NO_x emissions when compared with hydrocarbon-only diesel fuel, with typical differences between fuels below 25% or negligible. Increased NO_x emissions with FAME are often explained by the higher combustion temperature due to the fuel-bound oxygen in FAME and by the shorter ignition delay (from the start of injection) providing time for smoother combustion reducing the NO_x emissions when compared with diesel fuel [170–176]. On-road studies have used high-cetane diesel fuel in comparison with FAME, while FAME has often a higher cetane number than marine fuels [170,177–179]. Besides fuel oxygen content and cetane number, viscosity, aromatic content, density, distillation range, saturation degree and chain length of fatty acids may affect the formation of the NO_x emissions with FAME. For example, high viscosity may deteriorate the atomization of the injected fuel. The effect of fuel on the NO_x emissions depends also on the design of the engine and injection system, as well as on the engine loads used in the testing protocol [180–182].

Non-esterified, upgraded straight oils and fats have been studied as marine fuels to some extent since these are feasible fuels for large

engines without transesterification to FAME. Typically, viscosity is substantially higher and cetane number lower for straight oils and fats when compared with diesel fuels. In one study, blending 30% of straight biofuel in diesel fuel did not change the NO_x emissions significantly [87].

Tyre pyrolysis oils, crude and distilled, have been reviewed by Mikulski et al. [183]. The NO_x emissions obtained with these fuels have shown discrepancy, however, in many cases, NO_x emissions were reduced at lower engine loads, while the opposite was observed at higher engine loads. Tyre oils tested contained e.g. aromatics and their cetane numbers were worse than those of FAME.

Water-in-diesel fuel emulsions (WiFE) containing 20% water have been developed to reduce NO_x emissions along with a reduced combustion temperature. Water is not soluble diesel fuel, and thus emulsifier additives are necessary to keep the emulsion homogenous. The WiFE has been used in HSD heavy-duty diesel engines [184,185] and also in marine diesel engines [186–188]. Mayer et al. [189] reported of achieved Tier III NO_x emissions with a water emulsion without an EGR or SCR system. The WiFE may increase the wear of the engine [190].

A summary of NO_x emissions is shown in Fig. 6a. NO_x emissions can be reduced mainly by aftertreatment (SCR), engine internal methods (e. g., EGR), and certain combinations of fuels and engine technologies (LNG, methanol, paraffinic diesel, water in diesel). Slight NO_x reduction is achieved also by SO_x scrubbers. For ammonia as a marine fuel, it is premature to deem whether the Tier III NO_x level is reached without aftertreatment.

4.3. Methane emissions

The combustion of hydrocarbon fuels is not perfect and hence hydrocarbon emissions, including methane, are formed from partially unburned fuel "slipping" from the combustion cycle. The design of the engine, combustion chamber, injection pressure and fuel mixing are examples of factors affecting the formation of methane emissions [191, 192].

Methane emissions are typically low for diesel engines and for methanol DF engines, for which methane emissions of 0.02 g/kWh have been reported for an 80% engine load [140]. Additionally, methane emissions below the detection limit have been observed using additised methanol in an HSD engine [162]. In contrast, substantial methane emissions from LNG-fuelled ships have been reported in conditions favouring incomplete combustion [159,193]. Methane is a strong greenhouse gas (GWP100 is 28) and control of methane slip is necessary for LNG engines [194]. With certain assumptions, methane emissions of approx. 5.8 g/kWh would compensate for the GHG mitigation potential of LNG when compared to HFO [90]. The FuelEU Maritime Initiative (within the "Fit for 55" package) defines the default downstream TtW emissions of the fuel lost as fugitive emissions (Cslip) as up to 3.1% of the mass of fuel for LNG DF engines depending on engine type (at 50% engine load). In a recent study [74], the ratio $\Delta CH_4/\Delta CO_2$ in the emissions from LNG vessels should be equal to or lower than 3.9% (volume-based) to correspond to the climatic forcing for 100 years caused by shipping fuelled by diesel. Authors here note that emission evaluations per CO_2 emission may be influenced by decreased energy efficiency.

On-engine development can significantly reduce methane slip. For example, high-pressure (HP) gas DF engines emit very low methane emissions at levels of 0.23 g/kWh [66,104,195]. Higher methane slip emissions are reported for low-pressure (LP) LNG DF engines. In the on-board measurement of an LPDF LNG engine, methane emissions have been reported on average to be 1.4 g/kWh at high engine loads, while up to 5–5.6 g/kWh at low engine loads [159]. Other reported methane emissions for LPDF LNG engines have been 6.2 g/kWh [195], 5.5 g/kWh and 3.8 g/kWh [104] [196]. In on-board measurements, methane levels have been reported as 3.7–25.5 g/kWh, with the highest emissions at a 25% engine load [197]. Even higher methane emissions have been

reported in a testbed related to a specific NG-fuelled engine [136]. As mentioned, high-pressure DF LNG engines emit low methane emissions. Cylinder deactivation technology is also an option to reduce methane emissions from LNG DF engines [197] amongst other potential developments.

One option to tackle methane slip from existing and new-build marine LNG engines is methane oxidation catalyst (MOC), which have already demonstrated 70–80% methane conversions [192]. However, further research is needed to solve the long-term performance of the methane catalyst systems on-board. Blending hydrogen to methane (hythane fuel) may reduce the methane slip along with lower CO_2 emissions and increased efficiency (accelerated combustion speed), albeit NO_x emissions tend to increase [107].

All in all, the methane slip from LNG engines is of concern, and it can be reduced using on-engine technologies (e.g., high-pressure technology, better fuel mixing, combustion chamber design, reducing crevices), by utilising MOC type aftertreatment systems, or by using hydrogen with methane.

4.4. NH_3, N_2O and formaldehyde emissions

NH_3 emissions from diesel engines are mainly related to urea-based SCR systems for NO_x control, although the highest NH_3 emissions are typical for three-way catalyst-equipped gasoline cars [198]. For marine engines, very low NH_3 emissions are reported. For example, in a study on-board a ship, NH_3 emissions were close to the detection limit downstream of the SCR ($NH_3 < 0.026$ g/kWh), and below the detection limit after an SCR and scrubber combination. NH_3 is water-soluble and may dissolve in scrubber water. Published NH_3 emissions downstream of SCR systems in marine engines are scarce. NH_3 emissions are harmful (see introduction) and deserve consideration when developing new emission control technologies for marine engines. In road transport, NH_3 is limited for example in Europe (max. 10 ppm on average for heavy-duty engines) and is anticipated to be considered for more stringent control under the future new standards.

N_2O emissions measured from marine engines have been below the detection limit of the instruments used in the reported studies (<0.04 g/kWh) [87]. However, N_2O emissions are known to be induced by the exhaust aftertreatment technologies used in road-transport, namely three-way catalysts for stoichiometric spark-ignited engines [198–202] and in the NO_x adsorber and selective catalytic reduction (SCR) for diesel engines [203,204]. The formation of N_2O depends on, e.g., the active metal of the catalyst, the reaction temperature, rich-to-lean transition, and exhaust composition. Hence, when developing new exhaust aftertreatment technologies for marine diesel engines, N_2O emissions may become relevant. The possible use of ammonia as fuel may require reducing both NH_3 and N_2O emissions simultaneously [50].

Formaldehyde emissions, as well as CO and HC emissions, are the products of incomplete combustion of carbon-containing fuel. These emissions from marine engines using residual or distillate fuels have been very low or below the detection limit of the measurement instruments used. Formaldehyde levels reported for MSD marine diesel engines have been for example 0.017–0.048 g/kWh (Supplementary Table S5). As a reference, the limit for formaldehyde emissions in the US for HDVs is 0.022 g/kWh. FAME content in diesel has not affected significantly carbonyl emissions with one marine diesel engine [176].

Scrubbers reportedly reduce HC emissions to levels lower than when using low-sulphur fuel [140].

Measurable formaldehyde emissions have been reported for NG-fuelled engines [159,192,197].

For methanol DF, the formaldehyde emission reported have been negligible (4.9×10^{-4} g/kWh) and also low for small alcohol diesel HSD engines using methanol additised with an ignition improver (0.004–0.014 g/kWh) [162]. Theoretically, the oxidation of methanol could lead to formaldehyde emissions. Emission of unburned methanol is of concern due to its toxicity.

4.5. Particulate matter emissions (including PAH and heavy metals)

PM mass emissions (and PAHs) form through the incomplete combustion of fuel (and lubricating oil). Particles are formed in the early phase of combustion, typically in the fuel spray where the fuel-to-air ratio is elevated. PM forms through the presence of alkynes and PAHs [183]. Heavy metals in exhaust PM originate from the fuel, engine, lubricating oil and engine wear.

Not only the PM mass emission, but also its composition and produced (ultrafine) particle number concentrations are important. Engine exhaust PM emissions contain BC (see the section later) with associated metallic ash, BrC and lighter organic compounds and, often hydrated, inorganic ions (sulphates, nitrates, ammonium salts etc.). PAHs, heavy metals, and other harmful organic and inorganic species are carried also on particle surfaces. BC emissions are climate-warming while sulphates, organics and nitrates are climate-cooling aerosol species [16]. The amount of sulphates, semi-volatile compounds (e.g. PAHs) and particle-bound water in PM depends on the engine, fuel and exhaust treatment technologies and also on the measuring conditions through aerosol processes during the cooling and dilution of the raw exhaust. For high-sulphur fuel, hydrated sulphuric acid and semi-volatile organic compounds condense on particles from the gas phase during diluted sampling, while a lower amount of these species is collected by using hot PM sampling procedures (e.g. in-stack). The repeatability of PM results and comparability between studies would require a stricter determination of the sampling conditions than standardised today (ISO 8178 standard) [205–208].

4.5.1. The effect of fuels on the PM, PAH and heavy metals

PM emissions can be significantly reduced by switching from residual fuels to distillates or other fuels, which have low sulfur and ash contents. When using residual fuels, PM contains substantially "heavy" species (e.g., BC, tar BrC, long-chain high-molecular-mass heavy organic compounds, sulphuric acid and combined water, metal sulphates, metal oxides), whereas these species are present to a lesser extent when using cleaner distillate fuels and biofuels [206,209]. PAHs, heavy metals and other harmful species carried on particle surfaces are formed to a lesser extent when fuels are clean in terms of their content of these species.

The PM emissions reported are high for marine engines using high-sulphur residual fuels, up to 1.5 g/kWh (ISO 8178 measurement method) (Fig. 6c, Fig. 7), while distillate fuels have shown PM emissions of below 0.1 g/kWh [87,140], which is largely related to the contribution of sulphates in PM. Fuel sulphur combustion product, SO_2, typically
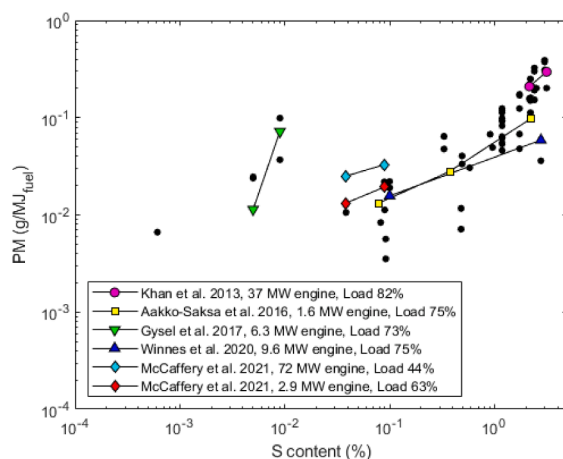

Fig. 7. The effect of fuel sulphur content on PM emissions. Lines combine the results obtained with different fuels in the same engine. References mentioned are [58,73,140,212,213] and rest are presented in the Supplementary material (Appendix S1).

forms 1–2% of SO_3, which further reacts to sulphuric acid and (metal) sulphates in PM with the ratio of conversion depending on engine load (see Fig. S2) [210]. An elevated air-to-fuel ratio, combustion temperature, and presence of vanadium (in fuel or SCR), for example, increase the conversion of SO_2 to SO_3 [211]. The fraction of hydrated sulfate in PM has been found 22%–62% for HFO fuel, while only 8.3% for MDO fuel. The conversion of fuel and lubricating oil originating sulphur into sulfate in PM increased from 0.4% to 3.7% as the engine load increased from 20% to 100% [59]. Even for marine fuels containing 0.5% sulphur, sulphates and combined water may remain the major constituents of PM.

Paraffinic sulphur-free fuels (HVO, GTL, XTL) reportedly reduce PM emissions even when compared with distillate fuels. These fuels are sulfur-free and they have high cetane numbers and hydrogen-to-carbon ratios. Studies of using paraffinic fuels in MSD or SSD marine diesel engines are sparse. A study comparing GTL to MGO in heavy-duty diesel engines found a decrease of 12–16% in PM emissions combined with a decrease in NO_x (up to 19%), CO (25%), and CO_2 (4%), and smoke emissions (30%) [168]. For on-ground HSD applications, PM emissions with paraffinic fuels generally reduce when compared to traditional diesel [166].

Oxygenated FAME biodiesel tends to reduce PM emissions since the fuel oxygen prohibits the formation of long carbon chains and enhances the oxidation of the initially formed PM [87], particularly in conditions where the fuel-to-air ratio is elevated. Additionally, FAME does not contain aromatics and PAHs, soot precursors. FAME use inhibits soot formation, and hence carbon surfaces for the adsorption of semi-volatile compounds [214]. PM reductions when using FAME in marine engines have been reported, e.g. reduction of 75% with fish oil FAME [172,176, 179]. One study found a 25% reduction in PM with a 50% FAME blend at high engine load, while at low engine load PM emission increased [176]. In on-road studies, PM reductions have been from 4% to 63% with FAME blends [176]. Although FAME reduces the soot part of PM, the soluble organic fraction of PM potentially increases due to heavy boiling compounds of FAME. Hence, PM emissions with FAME may be elevated e.g. at low loads or cold exhaust (and sampling) temperatures. This effect can be reduced by DOC to achieve low PM emissions [215,216]. Tyre pyrolysis oil contains aromatics, and is suspected of increasing PM emissions when compared with diesel fuel, which is also indicated in some studies [183].

Methane and methanol do not contain any carbon-carbon bonds and are expected to lead to low PM emissions. This has been evidenced for LNG DF engines, which emit very low PM emissions, for example approx. 0.02 g/kWh, which is more than one order of magnitude lower than that for diesel engines [136,217]. For 4.3 MW LNG DF engines, organic PM emissions (0.0044 g/kWh) are reportedly greater than BC emissions (0.0008 g/kWh) [158]. LNG does not contain heavy metals, but metal-oxide particles originating from lubricating oil combustion have been reported for LNG DF engines [218]. The metallic elements have been found as both internally and externally mixed with BC [219].

Methanol use leads to relatively low PM emissions, for example, 0.093 g/kWh for a DF engine at an 80% engine load [220]. For a smaller alcohol diesel HSD engine on methanol additised with an ignition improver, PM emissions were 0.045 g/kWh, which is the same level as PM emissions observed for low sulphur distillate fuels used in marine diesel engines [162].

High PAH emissions for residual fuel use in marine diesel engines have been reported (Table 4) [87,140,221] and substantially V, Ni, Fe, Ca, and Na. Ca is the dominant metal in engine lubricating oil for large marine engines. These species observed in PM emissions have been low for low-sulphur fuels [87,218,221]. For FAME, in line with the absence of PAHs in fuel, reduced PAH emissions are reported in comparison with diesel fuel [222].

4.5.2. The effect of exhaust aftertreatment on PM emissions

SO_x scrubbers, SCR, and DOC may remove PM to some extent. For

Table 4

Emission factors for gaseous species, PAHs (BbP, BkF, BaP=Bentzo(x)Pyrene, IP=Indeno [1,2,3-cd]pyrene) and metals in PM emissions for MSD and SSD marine engines using residual and distillate fuels. More details are in Supplementary Tables S4 and S5.

Species	Residual fuel	Distillate fuel
	(g/MJ)	(g/MJ)
CO_2	61–81	75–81
SO_2	0.29–1.2	0.04–0.25
CO	0.057–0.255	0.074–0.202
THC	0.018–0.057	0.026–0.068
	(mg/MJ)	(mg/MJ)
CH_4	<0.6–6	<0.4–1
Formaldehyde	<2.5–7	<2.1–4
NH_3	<0.2–1.2	<0.5–1.3
N_2O	<0.8–4	<2.1–4
BC	<1.7–5[a]/3–6[b]	<1.6–2.4[a]/2–14[b]
	(µg/MJ)	(µg/MJ)
BbP	<0.61–1.5	<0.14–0.31
BkF	<0.37–0.73	<0.12–0.29
BaP	<0.02–0.5	<0.05
IP	<0.14–0.37	<0.02
Sum of 7 PAHs	<2.4–17.1	<1.2–4.8
Sum of 16 PAHs	24–94[a]/148–525	40–84/–
As	<0.24–1.5	<0.24–0.96
Cd	<0.24/2–4.7[b]	<0.24
Cr	<2–9.8	<2.2–4
Cu	<4.9–9	<1–4.9
Ni	<192–424[a]/ <778–1015[b]	0.2–24; 95.2[c]
Pb	0.7–5; 14.6[c]	0.2–2.6
Se	0.2–0.7	0.2–0.5
Zn	<0.24–39[a]/32–61	<0.24–23
V	1220–1924[a]/<4146[b]	<5[a]/12–47.6[b]

[a] Below 15 MW.
[b] Above 15 MW.
[c] Highest result reported.

example, a 17–45% reduction can be achieved by using a scrubber depending on the used engine and fuel [60,140,223]. However, this effect is not consistent in all studies, which may be related to the different scrubber types, and partly to the sampling methods [140,144]. The amount of H_2SO_4 and associated water condensed on the PM increases as the dilution ratio and temperature decrease. Cold and wet exhaust after the scrubber may require probe heating, and if probe heating is not used before the scrubber, the PM may seem to decline. A scrubber captures H_2SO_4 and bound water, however, once sulphuric acid condenses in PM (or nucleates), it will not evaporate easily due to its high boiling point of 337 °C. In addition to sulphur species, the scrubber liquid could capture the exhaust's soluble organic and inorganic compounds (also metal oxides), or these species could condense on the PM [206]. SCR and DOC may reduce PM emissions by oxidising the organic fraction [139,141,156,224,225]. On the other hand, oxidation of sulfur of fuel in catalysts tend to form SO_3, which generates sulphates in PM [176]. A recent study reported lower PAH emissions for low-sulphur fuel than when using a scrubber and HFO, except for heavier PAHs [140]. With scrubbers, using residual fuels leads to high PAH emissions in the air and aquatic ecosystem. Teuchies et al. [226] found that scrubber washwater was acidic and contained e.g. Zn, V, Cu, Ni, phenanthrene, naphthalene, fluorene and fluoranthene. The scrubbers' discharge washwater is acutely toxic for aquatic organisms. Several 'priority hazardous substances' (Water Framework Directive) are already exceeded in the docks and the Scheldt estuary.

An on-board study reported a DOC efficiently reducing heavy metals present in PM for residual fuel use, indicating the PM capturing property of this DOC type [139,141]. Another on-board study with a SO_x scrubber did not observe reductions in metal emissions (e.g., Ni 0.5 mg/m³ STP before/after scrubber), while the metal emissions were low with a low-sulphur fuel (e.g., Ni non-detectable) [60]. Heavy elements in residual fuel increase the effective density of the particles [218].

4.5.3. The PM composition in different particle sizes

The PM compositional species are present in different particle sizes. For 20.2 MW diesel engines, particles below 1 µm have been found to contain V, Ni and S, while particles above 200 nm contained Ca, V, and Ni. Unburned fuel and lubricating oil originating OC was observed in particles at 100 nm [227]. Lubricating oil as a source of PM emissions is particularly important when the PM originating from the fuel is low.

Nucleation mode particles consist of sulfates, organic compounds, ash and carbonaceous particles. For sulfur-free fuels, the nucleation particles are assumedly dominated by hydrocarbons [176] For diesel engines (MSD 1 MW) the finest particles reportedly originated from the fuel, while the larger particles contained elements derived from the lubricating oil [228].

For LNG DF engines (4.3 MW), OC has been found to originate from the lubricating oil and PN below 10 nm from lubricating oil metals [158]. In another study for an LNG DF engine, the non-volatile particles were fuel-originated at <10 nm, while particles originating from lubricating oil were 10–30 nm, and stain-like nucleation particles together with the grown core particles were 20−30 nm [229].

4.6. Particle number emissions

Particle number emissions depend on engine, fuel, lubricating oil, exhaust aftertreatment and measurement conditions, amongst others. PN emission results depend on the chosen sampling and measurement methods, similarly to PM emissions. Legislative limits for inland waterways refer to solid, non-volatile particles PNnv emissions for particle size ranges above 23 nm (abbreviated here PNnv>23), which is less sensitive to the sampling conditions and measurement system than the total particle number emissions (PNtot). For PNtot, the variable presence of volatile and semi-volatile particles depends on many parameters, e.g. exhaust temperature, the sampling methods used and particle size ranges measured. Different research studies may report various types of PN emissions.

For marine MSD diesel engines, with or without exhaust aftertreatment, using residual (0.7 and 2.2%S) or distillate fuels, PNnv > 23 emissions have been reported from 0.6×10^{14} 1/kWh to 3.5×10^{14} 1/kWh (Fig. 6d) [136,230]. Modern diesel engines are potentially in the lower part of the range.

Reduced PNnv > 23 emissions were found when moving from fossil marine fuel oil to biofuels, while PN emissions did not change for a 0.4 MW 1-cylinder engine (MGO < 0.1%S; fuel oil 2.17%S) (Petzold et al. in [103]). An HSD engine showed only small differences in PN emissions when comparing a fuel oil (0.12%S) and MDO fuels [231].

The effect of scrubbers on PNnv>23 emissions is not consistent in different studies. A scrubber did not change the PNnv>23 levels for one engine, while for another engine the decrease was approx. 30% at a 75% engine load. PNnv>23 emissions were lower for MGO than downstream of the scrubber with HFO fuel [136]. In one study, PNnv>5.6 was reduced by 48% with a scrubber [143], while in another study no clear reducing effect of a scrubber on PNnv>23 emissions was observed [140]. In the literature, engines and vehicles have emitted non-volatile sub-23 nm particles [208].

For LNG DF engines, the PNnv > 23 emissions reported are remarkably low, for example, PNnv > 23 emissions of 1.3×10^{12} 1/kWh [136].

4.6.1. Total PN emissions

High PNtot emissions (including volatile PN) of 2.1×10^{16} 1/kWh have been reported for an MSD diesel engine equipped with SCR (low-sulfur residual fuel, 75% engine load). About 50% PNtot was found to have a non-volatile core at 250 °C [224]. Lower PNtot emissions have been reported for Bio-FA blend (30%) in fossil fuel and for low sulphur fuel (<0.1%S) than for residual fuel [232].

For paraffinic and biofuels, studies are available mainly for HSD engines. A slight increase in PN emissions has been reported when

moving from MGO to paraffinic GTL fuel [168] and FAME biodiesel assumedly due to reduced particle sizes (Jayaram et al. in [103]).

In the scrubber study, PNtot emissions were reduced by 79% (75% engine load), potentially related to the tendency of hydrophilic particles to transfer into the scrubber liquid or collide in water droplets [140]. PNtot reportedly reduces by using scrubbers by as much as 92% [143] and 70–90% [232].

For an LNG DF, Anderson et al. [159] reported PNtot emissions of only 5×10^{12} 1/kWh. On the other hand, Corbin et al. [158] noted that the majority of particles emitted from an LNG DF engine were in the size class below 23 nm, hence, not detected with instruments designed for PN>23 nm. Indeed, PNtot emissions reported were over 10^{13} 1/kWh. Alanen et al. [229] reported PNtot emissions of 2.7×10^{15}–7.1×10^{15} 1/kWh at a size range of $1.2 - 414$ nm for a 1.4 MW DF engine using NG and marine distillates. When the smallest particles are considered, PNtot emissions from LNG DF engines increase and potentially deserve to be filtrated [229,232]. However, particle number emissions for different fuels and aftertreatment devices are sparse and more studies are required as new fuels enter the arena.

4.6.2. Particle size distributions

Particle size distributions for residual fuels have been reported to be unimodal (two overlapping modes). For distillate, paraffins and bio-diesel fuels, the bimodal particle size distributions are reported with carbonaceous accumulation mode and ash related nucleation mode (<50 nm) (also semi-volatiles from lubricating oil) [172]. For FAME, a lower number of particles in the accumulation (soot) mode are reported than for conventional diesel, while an increase in nucleation mode particles with FAME may be seen [176,216,233] related to insufficient solid carbonaceous agglomerates to adsorb volatile hydrocarbons [234].

4.7. Black carbon emissions

BC is an important contributor to global warming, and it adversely affects health and the environment (see introduction). The fraction of BC in PM and composition of PM varies for different engines, fuel and aftertreatment technologies. Hence, merely regulating PM emissions will not necessarily reduce BC, depending on the PM reduction technology considered.

The IMO has worked since 2011 on the consideration of the impact of BC emissions from international shipping on the Arctic (Marine Environment Protection Committee, MEPC 62). The International Council on Clean Transportation (ICCT) has organised BC Workshops, including consideration of efficient BC control methods. For regulating BC emissions, an agreed measurement methodology is needed. In 2015 (MEPC 68), the IMO agreed on a BC definition according to Bond et al. [235]: BC forms from the incomplete combustion of carbonaceous matter and it is non-volatile, non-water-soluble, light-absorbing, 10–90 nm spherules that contain more than 80% carbon in double bonded forms, and form aggregates immediately after formation [235–237]. In 2018, three candidate methods for the BC measurements were selected by the IMO. These were the: photoacoustic spectroscopy (PAS), laser induced incandescence (LII) and filter smoke number (FSN) methods (the Sub-Committee on Pollution Prevention and Response, PPR 5). BC can be measured using optical methods based on filter blackening (e.g., smoke meters, aethalometers, multiangle absorption photometry (MAAP)), filter-free optical methods (e.g. PAS) and methods based on refractory properties (e.g., LII). Elemental carbon (EC), which is not commensurable with BC in the shipping sector, is measured using thermal-optical (TOA) methods [87,158,238,239]. Using a nomenclature such as refractory BC (rBC) reveals the principle used for measurements [238]. All these measurement methods have their limitations related to definitions of the carbon measured and sensitivity towards interferences. The optical BC measurement methods are sensitive to aerosol or gaseous species affecting the coefficients for converting the light absorption into a BC mass concentration. The non-BC light

absorbing aerosol species include brown carbon (BrC), mineral dust [54, 237,238,240,241]. The difference between BC and BrC is smooth, and their differentiation by measurements is challenging [242–244]. Some measurement methods account for tar BrC as BC, while others do not, and, given the potentially high fraction of tar BrC at lower loads with residual fuels, this effect should be considered, especially when sub-optimal engine loads are studied [158,209]. Light-absorbing compounds, including BrC, cause radiative forcing in the atmosphere and induce global warming. Coating of particles and particle size also affect the light-absorption properties of aerosol [240,245–248]. Ideally, the exhaust sample would represent aerosol after the atmospheric reactions, which is not the case after the sampling systems without chambers to simulate secondary aerosols [139].

Some artefacts, direct or indirect, are known for BC measurement techniques. Filter-based methods suffer from the effect of aerosols accumulated on the filter and from scattering. The latter is avoided by MAAP detecting the transmitted and backscattered light. Filter related artefacts are avoided by filter-free methods, for example, PAS and LII [54,238,247–249], which are however vulnerable towards interferences reflected from the calibration. For example, when calibrated with the TOA method, some constituents from residual fuels interfere with the results [206]. Additional uncertainties are considered when dilution systems are needed, especially for very high dilution levels, for example when devices designed for atmospheric measurements are used for measuring high BC concentrations (in atmospheric studies these instruments measure without dilution) [87]. Variation in the BC results obtained with different measurement methods are reported as 11% (30 $\pm$3.3 mg/kWh) in a study by Corbin et al. [158] and 10% at BC emission levels of <30 mg/kWh, with greater variation at higher BC concentrations [21,87,250–253].

Many IMO and ICCT documents and results from voluntary ship BC projects called by the IMO (see supplementary material) have been published in recent years. BC emission levels for different types of marine engines, engine loads and fuels used are high, as reflected in the BC emission inventories. For example, wide variation in BC emission factors have been observed, on average from 0.03 to 0.22 g/kWh [21,51,235, 250–255]. Comer et al. [51] modelled a fleet-wide average BC emission factor of 0.050 g/kWh (appr 6.1 mg/MJ). Assumedly, the higher BC emission factors are related to data on older engines and low engine loads, since modern marine diesel engines at high engine loads have shown BC emissions at low levels of 0.02 g/kWh [60]. The BC emissions vary within four orders of magnitude for different ships using distillate fuels only, as seen in Fig. 6b. Hence, comparison of BC emissions for different diesel-type fuels should be based on the measurements on the same representative engine, since otherwise, differences in BC emission levels of different engines may hide the effect of the fuels (Figs. 8a and S3b). Evidently, BC emissions are important for marine engines of all sizes, since large engines emit less BC per fuel consumed, but consume orders of magnitude more fuel than smaller engines (Figs. 2 and 3).

Mitigating the BC emissions from marine engines may involve modifying the fuel, engine (or both), or adapting the exhaust aftertreatment technology. Switching from current residual fuels to clean diesel-type fuels is a tempting option due to its simplicity and immediate impact on a large scale (retrofitting). However, the achieved reductions in BC emissions tend to be modest, at approx. 30% [256–258] and variation in the results is high with even increases observed (e.g. a 6 MW engine in [259]).

An interesting fuel is the one meeting the global 0.5% fuel sulphur limit of 2020. One study with an MSD engine switched fuels from 2.5% to 0.5% to 0.1% sulphur contents and found a respective decrease in BC emissions at high engine loads (from 0.032 to 0.013 to 0.011 g/kWh), but the highest BC emissions for 0.5%S fuel at low engine loads (from 0.104 to 0.204 to 0.094 g/kWh) [87]. A sulphur limit of 0.5% does not prevent using residual fuel components while meeting a sulphur limit of 0.1% in practice requires distillates. In the cited study, the 0.5%S fuel contained asphaltenes (5.7 wt%), while the 0.1%S fuel contained high
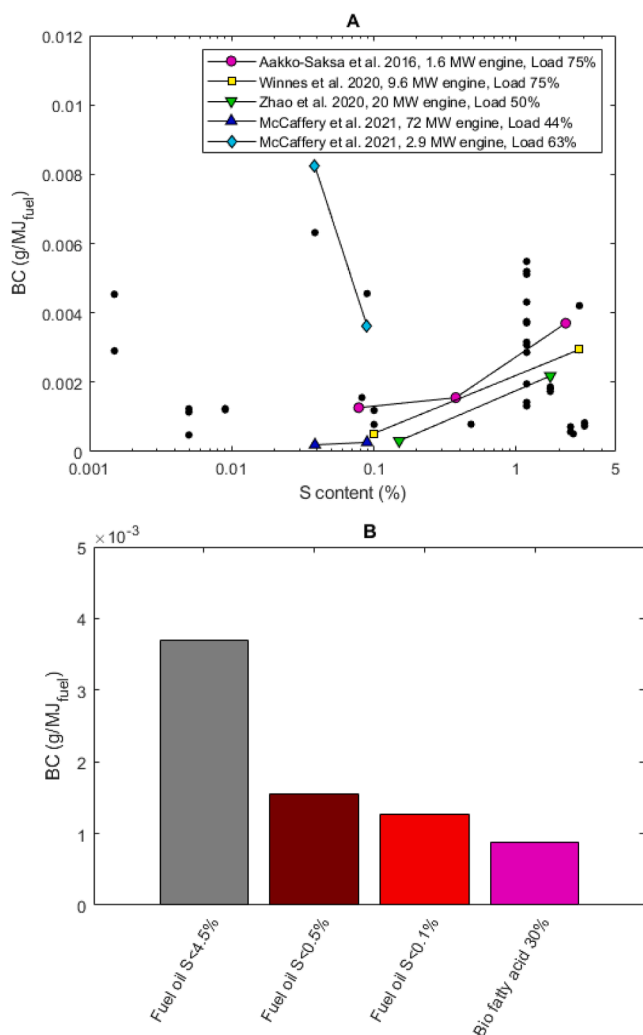
Fig. 8. Comparison of fuel oils a) $S < 4.5\%$, $S < 0.1$, in which lines combine the results obtained in the same engine while dots are individual results from different engines b) $S < 4.5\%$, $S < 0.5\%$, $S < 0.1$ and bio fatty acid (30% blend with diesel fuel) from studies, in which several fuels were used in the same engine at engine loads equal or above 40%. The bars represent median values. References mentioned are [59,87,140,213] and rest are presented in the Supplementary material (Appendix S1).

amounts of aromatics (42.6 wt%) without asphaltenes. The hydrogen contents were at the same level in these fuels (hydrogen 12.9 and 12.5 wt%). The 2.5%S fuel had the highest content of asphaltenes (28.3 wt%) (see supplementary Tables S11 and S12). The considerations are as follows:

- High BC emissions for 0.5%S fuel at low engine loads may be related mainly to its asphaltene contents due to incomplete combustion at insufficient temperatures, while lower BC emissions for 2.5%S could be related to vanadium acting as "fuel-borne catalysts" [260]. Metals are even considered to be used in fuel additives (e.g., Ce, Pt) in combination with catalysts [225]. However, many metals are toxic and not desired in breathable air.
- The aromatic content of 0.1%S distillate fuel was notably high without increased BC emissions. PAHs (di+ aromatics) rather than the total aromatic content of fuel are known to increase soot formation, and hence the PAH content of road diesel fuel is limited in the EU [261–268,].
- The high sulphur content of residual fuel is associated with asphaltenes. Hence, reducing the fuel sulphur content by blending residual

with distillate fuels or by refining residual fuel tends to decrease its asphaltene content.

Engines with a modern fuel injection system could be less sensitive to fuel changes than old engines equipped with mechanical fuel injection systems used in the above mentioned study due to e.g. the impact of viscosity and density of fuel on the start of injection and spray formation [165]. For example, on a newly constructed cargo vessel switching from HFO to MDO reduced the BC emissions up to 74% and 85% at low (20%) and high (50%) engine loads (DMD-MAN B&W 6S70ME-C8.2) [59].

Of particular interest are paraffinic renewable fuels (HVO, BTL, e-diesel). Paraffinic fuels have been studied mainly in HSD diesel engines. For inland ships, PM reductions of 16 to 60% and black smoke reduction of 32% have been reported when comparing paraffinic diesel (GTL) with road diesel fuel (EN590) [269]. In contrast, a plume study on an HSD engine showed increased BC emissions with paraffinic HVO compared to ultra-low sulphur diesel [169]. These contradictory results could be due to different measurement principles, engines, test set-ups and fuel properties. Many studies of on-road heavy-duty HDS applications have shown lower soot emissions for paraffinic fuels than for conventional diesel fuels [166]. This is also expected from a fuel-to-soot chemistry point of view.

Oxygen-containing FAME-type biofuels exhibit decreased PM and soot emissions in road and non-road HSD applications [166,171,215]. Similar findings have been observed for marine engines as shown in Fig. 8b including the BC results from studies where different fuels were used in the same MSD engine at engine loads above 40%. This approach enables a comparison of fuel effects without bias resulting from different BC emission levels from the engine types and loads used. In a study with an MSD engine, a non-esterified Bio-FA biofuel blend (30%) in fossil fuel showed a reduction in BC emissions when compared with residual and distillate fuels at high and low engine loads (BC 0.008 and 0.048 g/kWh) [87]. Another study found up to 30% lower BC emissions for palm oil and animal fat than for MGO, but higher BC emissions for soybean and sunflower oils [54]. For FAME, BC emissions may decrease even when the PM emissions increase if the PM contains elevated levels of organic carbon [215]. FAME-type biodiesel (ULSF, soybean blends B20, B50) reduced PM and BC emissions by 20–42% in a marine diesel engine at a 75% load (Jayaram et al. in [103]).

LNG DF engines emit almost negligible BC emissions, more than three orders of magnitude lower than those reported for high-emitting diesel engines. The BC emission measurement results reported for LNG DF engines are available from EUROMOT data, in which NG used as a main fuel in the DF engines exhibited low BC emissions in all engine size categories tested (below 0.0014 g/kWh at high engine loads, in one case, 0.017 g/kWh) [223,271]. Corbin et al. [158] reported BC emissions of 0.0008 g/kWh for a 4.3 MW LNG DF engine and concluded that the BC mostly originated from diesel pilot fuel. Alanen et al. [229] also reported low soot emissions for NG combustion and the contribution of the lubricating oil to particle formation.

Methanol can be clean-burning as it contains oxygen and only one carbon atom and it is a mono-molecular fuel. Stojcevski [270] reported reduced BC emissions when using methanol instead of distillate fuel as the main fuel in a DF engine. BC emissions were reduced by 55–75% depending on the pilot fuel injection when compared with distillate fuel. In the study by Diericks [112], in DF methanol operation, the brake thermal efficiency was reported to increase by 12%. The diesel substitution by methanol (energy ratio) was 67–70%. The average decrease in specific NO emissions was 61% and in specific soot emissions 77%. Specific emissions (per kWh) take into account differences in fuel energy contents. BC emissions in the same study were 0.028–0.191 g/MJ methanol fuel at 1250–2000 1/min. One concept reported is a methanol DF engine with water addition [189]. When diesel fuel is the main fuel in methanol DF engines, BC emissions correspond to those of diesel engines.

Water-in-fuel emulsion, WiFE (designed for NO_x reduction) may

reduce BC emissions in engines equipped with conventional fuel injection at low engine loads, while the benefit may be modest in modern engines [103,147,272]. A recent study by Mayer et al. [189] reported increased soot emissions at higher loads for a water/diesel emulsion (ME-LGIM DF, 7.12 MW). However, reductions in smoke opacity by WiFE have been reported [186,187].

BC reductions by SO_x scrubbers, SCR and DOC are not effective by default, since scrubbers are designed for reducing other emission species. In a study by Winnes et al. [140], BC emissions were reduced when using HFO and SO_x scrubbers, however, this BC emission was 1.5–4 times higher than that when using low-sulphur fuel oil without a scrubber. Alfa Laval reported the results of testing on a test-bed showing that their scrubber reduced BC emissions (IMO PPR 6 INF. 13) [273] and later BC emissions were also reduced in on-board ships measurements [144,274]. More details on SO_x scrubber studies are presented in the Supplementary material.

PM scrubber technologies combined with electrostatic precipitators (ESP) and bag filters are used in some large land-based industrial plants. When compared to wet scrubbers, ESPs and bag filters are larger and more expensive, although the waste gas flow rates and temperatures are lower and they do not form a sludge that requires treatment. ESP developments include wet electrostatic scrubbers (WES), Heterogeneous Condensation Scrubbers and bubble towers (BT) [103]. These need a wash-water treatment unit. WES increases particle charging by using sprayed droplets as diffused particle collectors, in place of ESP plates [103]. A new ESP system design has been developed for marine diesel engines (Usui Co.) [275,276]. In this ESP system, the exhaust gas flow rate design is higher than traditional and the back-pressure is low [277]. In 2021, the Wet Electrostatic Precipitator (WESP) by Ecospray was announced to be installed on a cruise ship [278]. Additionally, Valmet announced the development of WESP technology to control exhaust particles, heavy metals, visible plumes, acid and oil mist [279]. Zukeran et al. [280,281] reported that PM emission removal efficiency with ESP exceeded 85% and the removal efficiency for the particulate PAHs in the ESP reached 97%.

ESP-based systems may achieve high BC reductions, however, they are large in size and electrical risks are considerable in installations. Storage and disposal of the removed PM are needed, enabling the recycling of e.g. metals. With ESP, energy consumption increases and material limitations may also lead to the need for flue gas cooling [147, 275].

Particulate filters are not compatible with residual marine fuels, mainly due to the ash and sulphur content of the fuel, while DPFs for 0.1%S marine fuels are being developed. Particulate filtration would efficiently reduce PM, PN and BC emissions when the fuel quality is adequate. DPFs designed for automotive diesel engines reduce emitted particles with an efficiency of more than 90%, provided that the fuel is sulphur-free diesel (below 0.001% sulphur content), but even then, filter clogging due to ash may be an issue. DPFs have small channels (micrometre range) where solid PM is collected and removed periodically during DPF regeneration [103,282,283]. The PNnv>23 limits in the European standards for diesel vehicles are met only with closed wall-flow DPFs. For the regeneration of DPFs, passive NO_2 assisted soot regeneration at relatively low temperatures (i.e. 250 °C), or active regeneration with oxygen (at approx. 600 °C) are common. However, using marine fuels containing sulphur, ash and other impurities leads to non-combustible metal oxides and sulphates, resulting in challenges with DPF regeneration strategies. The oxidation function in DPF systems generates NO_2 on purpose to enhance soot combustion, and harmful NO_2 may slip at low engine-out soot concentrations. The NO_2/NO_x shares are regulated for ground transport retrofit catalysts e.g. in the US and Europe [284].

The particle filter designs demonstrated for marine diesel engines include a ceramic filter system installed in auxiliary engines on 10 Pure Car Carriers to prevent new cars from fouling due to acid particulates during the loading and unloading of cars at ports (NGK Ceralec) [275,

285]. An early demonstration of PF was conducted on a ferry in 2012 (Mitsui O.S.K.) (ref in [103]). Additionally, a demonstration with an integrated particle filter and SCR system on an inland ferry using marine diesel with sulphur content below 0.1% has been conducted (Dinex F-SCR) [286]. Another prototype technology that has been demonstrated is multi-catalytic soot filtration for marine applications (ECO-Jet) [287]. Recently, an Exilator DPF system installed on the engines of a Danish ferry showed a reduction efficiency of over 99% for PM and PN, and also a significant noise reduction [288]. Installations of DPFs in Danish ferries have continued with the PureFilter system. DPFs designed for on-road diesel engines have been tested for auxiliary marine engines when using sulphur-free diesel fuel (S<15 mg/kg) [225].

The main challenge of using particulate filters is related to the sulphur and ash content present in marine fuels worsening, e.g., the operation, regeneration and long-term durability of the filters. The sulphur limit of 0.5% for marine fuels is not sufficiently low for DPFs, since ash-containing residual fuel components can be still present along with catalyst fines (Al, Si) [86], and even 0.1% sulphur-containing marine fuel is challenging. With future carbon-neutral fuels, barriers related to fuel cleanliness are likely to be alleviated depending on fossil fuel quality used for blending. Overall, technical challenges in exhaust filtration for marine engines are related to the regeneration of filters, additional energy consumption, exhaust gas temperature and back-pressure, reliability, durability and the space needed for the filter [103,147,275,287].

5. Discussion on opportunities and future prospects

5.1. Carbon-neutral fuels to mitigate GHG emissions

Carbon-neutral fuels for marine engines could help to meet the IMO's strategy to mitigate shipping's GHG emissions as an important piece in shorter-term solutions along with energy savings, system changes and emerging technologies. Tackling climate change is not enough: while exhaust emissions from ships also need to be at harmless levels for living organisms, human health and the whole environment. Combining carbon-neutral fuels with appropriate emission control technologies, (near-)zero exhaust emissions are achievable. The carbon intensity of fuels needs to be truly low to mitigate global warming, although each individual fuel batch does not need to be carbon neutral per se, if the fuel pool consists of very low-carbon and even carbon-negative fuels. The latter can be fulfilled if raw materials would otherwise degrade to GHGs or if carbonaceous by-products are to be permanently stored. The requirements for fuels accounted for as the low-carbon or carbon-neutral fuels are becoming ever more stringent. For example, at least a 65% reduction of WtW CO_2 emissions has been specified in RED II. The gradually increasing demand for carbon-neutral fuels improve their production methods and will increase their production volumes so that affordable prices of such fuels could become reality. Carbon taxes and policy instruments support this development. Processes for the production of such fuels are in principle available, albeit development is needed to utilise the most demanding raw materials, to increase the energy efficiency of the processes and to optimise the whole value chain (e.g. through electrolysis). Excess energy used by clean technologies may be compensated by using high-efficiency engines and heat recovery systems.

Carbon-neutral fuels produced from biomass, waste or renewable electricity-generated hydrogen could replace fossil marine fuels as "drop-ins" when resembling diesel, LNG, or methanol (Fig. 9). These fuels could replace their fossil counterparts overnight provided that such fuels become available at large quantities, because they would require minimal engine adjustments, if any. Of these, only methanol is biodegradable and has low toxicity to aquatic life, although it is toxic to humans [289,290]. E-fuels are actually irreversible hydrogen storages and circulate the carbon when captured CO_2 from flue gas or air is used in fuel production (CCU concept) and hydrogen is produced using
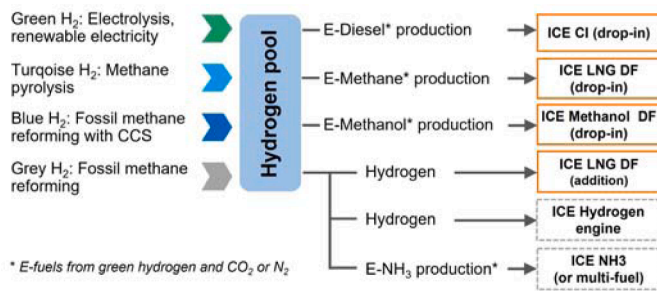
Fig. 9. Hydrogen pathways for ICE include fuels compatible with common diesel and gas engines (hydrogen-based e-fuels as drop-in). Hydrogen and ammonia ICE engines are not on market for marine applications, yet (marked with a dashed line).

electrical power generated utilizing renewable energy sources (green hydrogen). For e-fuel production, regional integration of fuel and hydrogen production with CO_2 capture involves challenging infrastructure needs. Carbon-neutrality of hydrogen and ammonia depends on their upstream emissions of production. For fossil fuels, the avoidance of CO_2 otherwise emitted could be realised by carbon capture on-board a ship. Engines for hydrogen or ammonia fuels may be introduced on market in the future. Hydrogen and ammonia could also be used as blends with conventional marine fuels, for example, hydrogen blending with methane (hythane) is a proven technology in the automotive sector. However, injection systems and hydrogen storage on-board are more challenging in shipping than in ground transport. When combining carbon capture on-board with carbon-neutral fuels (see Section 3.1), very low emissions could be achieved. Capturing carbon of electro-methanol on-board and pre-combustion of hydrogen could reduce up to 97% of CO_2 and over 80% of NO_x emissions and eliminate SO_x and PM emissions [74,75].

5.2. Cleanliness of exhaust promotes the use of renewable fuels

Carbon-neutral fuels otherwise chemically resembling fossil marine fuels of today, only with the absence of harmful constituents such as sulphur, asphaltenes or heavy metals, enable the use of the most efficient exhaust aftertreatment technologies to clean exhaust. How clean can marine engines be when using carbon-neutral "drop-in" methane, methanol and diesel-type fuels?

LNG DF engines emit extremely low levels of SO_x and PM emissions, and NO_x emissions can be low depending on the combustion cycle, even without exhaust aftertreatment. Technologies to control the methane slip emissions from LNG engines exist (HPDF) or are promising (e.g., MOC aftertreatment). Methanol is a clean-burning fuel, although its emission reduction potential concerning NO_x and PM emissions is lower than that for LNG, however, depending on the combustion technology selected. Methane slip is not of concern for methanol fuel combustion. Despite low NO_x emissions with LNG and methanol, even lower NO_x emissions are achievable when adopting the SCR system. For DF engines using diesel fuel as back-up, an SCR system is well justified.

Particle emissions (PM, PN, BC) are amongst the most harmful emission species, and these emissions exist also for LNG and methanol DF, so further reduction of particle emissions is necessary with exhaust aftertreatment. Efficient DPF technology is an option which is compatible with clean carbon-neutral marine fuels unlike with present high-ash ones. Carbon-neutral methane, methanol and diesel-type fuels combined with the best marine engine technology, and exhaust aftertreatment (SCR, DPF, MOC) would provide (near-)zero-emission shipping operations as regards known emission species. For considering ammonia as a marine fuel, abatement of N_2O, a strong GHG, will be one of the major challenges.

5.3. External costs of emissions justify investments in the production of carbon-neutral, clean fuels

The drivers for clean shipping are strong, but how can these benefits be valued? One possibility is to calculate the indirect, external costs caused by shipping emissions on society through the adverse impacts on health, the environment and the climate. The lifetime costs of exhaust emissions have been defined for vehicles and maritime transport (Directive 2009/33/EC) [291–294] (see Supplementary Table S12). For maritime transport, external costs have been evaluated in the Atlantic, Baltic, Black Sea, Mediterranean and the North Sea covering the health effects, crop loss, biodiversity loss and material damage. The lowest costs are for the Atlantic and the highest for the North Sea.

The external costs estimated in literature for emissions were used in this study to calculate examples of external costs for selected marine fuels. The selected costs represent in most cases the high estimates for maritime transport. The external costs selected from literature for climate-forcing emissions (CO_2, BC, CH_4 and N_2O) were as follows:

- CO_2: €77 per tonne emission [295], which is higher than the typical cost for CO_2 today.
- BC and CH_4 emissions are converted to CO_2eq emissions by using GWP factors. For BC, a GWP100 value used was 900 and a GWP20 value was of 1600. Higher and lower GWP values have also been estimated for BC emissions from shipping [235,296,297]. For CH4, GWP100 of 28 and GWP20 of 84 are reported.
- Global warming through the CH_4-induced formation of tropospheric ozone was not taken into account. N_2O was also not considered as it is minor emission from shipping today (GWP100 of 265).

External costs for emission species harmful to health and the environment are presented below (references in supplementary Table S12).

- NO_x €10,700 per tonne emission.
- SO_2 €10,500 per tonne emission.
- PM2.5 €34,400 per tonne emission. A meta-analysis by Gren et al. [298] found that external costs for PM2.5 were six times higher than those for NO_x and SO_x. In this study, the respective ratio is approximately three.
- NMHC €2300 per tonne emission.
- For PN and BC emissions, external costs related to health effects are not defined (see above for climate impact of BC).
- Hydrocarbons inducing e.g. tropospheric ozone were not taken into account.

Using the external costs listed, examples of external costs caused by emissions for present and clean marine technology choices are shown in Fig. 10. Using 260 Mtoe of residual marine fuels at Tier 0/I emission
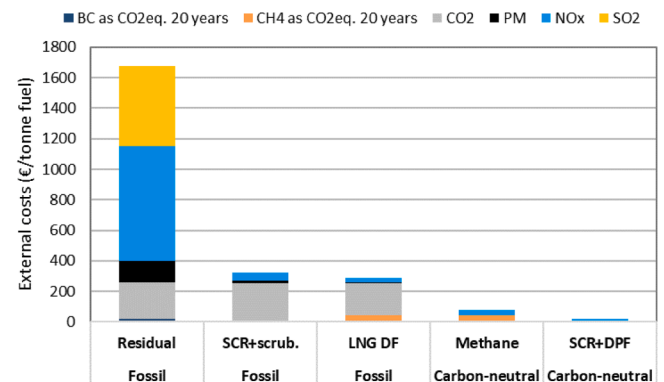
Fig. 10. Examples of external costs of ship emissions with selected technologies. For methane and BC emissions, GWP20 values were used.

levels would cause external costs of 433 billion euros annually with assumptions described (Am billion = 10^9). Maffii et al. [299] estimated external costs of 260 billion euros for GHG and air quality pollutants from the world maritime fleet in 2006. The difference between estimates in the two studies is due to the selected lower and upper end of external costs reported for maritime transport (Table S12). Notably, external costs of pollution from shipping are almost totally related to these emissions to air, since sewage and permitted oil spills represent only 0.25% of the total according to Maffii et al. [299]. These external costs could be avoided by using modern marine engines, carbon-neutral fuels and the best exhaust aftertreatment options. External costs here are likely rather underestimated than overestimated, e.g., for CO_2 emission when considering the recent natural disasters caused by climate change.

The costs of producing carbon-neutral fuels are high. However, the 2020 fuel sulphur regulations have already smoothened the difference between fossil and renewable or carbon-neutral technologies. Some of the common renewable fuels today are at a price level close to distillate fuels while producing advanced renewable fuels or electro-fuels is more expensive. Grey et al. [1] presented the following ranges of costs for various fuels (excluding infrastructure costs):

- Fossil HFO 36 €/MWh, fossil diesel 109 €/MWh, LNG 38 €/MWh
- Biomethane 91–144 €/MWh, biomethanol 75–144 €/MWh, HVO 140–195 €/MWh
- E-Hydrogen 110–200 €/MWh, e-methane and e-methanol 120–680 €/MWh, e-diesel 130–770 €/MWh .

Uncertainty is high regarding the cost estimates for emerging fuels. Producing e-fuels is always more expensive than producing e-hydrogen and proportional to the renewable electricity price. Hannula [300] has estimated that the production costs of e-methane could be 1.5–2.5 times higher than those of e-hydrogen, while e-methanol would be slightly more costly, and e-diesel (Fischer-Tropsch) approx. 1.4 times more expensive than e-methane due to the higher capital investment and lower efficiency. When considering additional storage and distribution costs, the differences in costs between liquid (diesel, methanol) and gaseous (methane) fuels narrows [300]. For e-fuels, also for hydrogen-derived e-ammonia, costs are dominated by the price of renewable electricity.

For any of the new carbon-neutral fuels, investments needed in the production are substantial, for example, an investment of 300 M€ for a new plant producing 0.3 Mtoe fuel would mean an investment of 300 billion euros in 1000 plants producing 300 Mtoe of fuels. This is a lower cost than the upper estimate of annual external costs for using residual marine fuels at Tier 0/I emission level ships. On the financing side, there is will to invest in solutions aligned with climate considerations, for example, the Poseidon Principles, an agreement introduced by a group of banks, integrates lending decisions to be in line with climate goals set by the IMO's GHG strategy [301]. Another example is the ETS system for shipping, which is already proposed in the European Union.

5.4. Which fuel to choose?

Modern marine diesel, gas DF or methanol DF engines with appropriate exhaust aftertreatment (e.g., SCR, DPF, MOC) are three solutions considered to achieve (near-)zero-emission shipping in the short-term, if fossil fuels are replaced by their carbon-neutral alternatives. An interesting question is which fuel type is the most reasonable for new fuel production plants considered. For some bio-based raw materials, the products are biomethane or biodiesel, while for e-fuels, the product fuel-type can be chosen.

A qualitative evaluation of the three e-fuels (e-methane, e-methanol and e-diesel) and as references fossil fuels and hydrogen/batteries, is shown in Table 5. The scores indicate the pros and cons for the best technologies identified concerning emissions into the atmosphere and infrastructure needs. Although this comparison is qualitative and

Table 5

Evaluation of impacts of assumed carbon-neutral e-methane, e-methanol and e-diesel as marine fuels with fossil and long-term references.

	SO_x	NO_x	PM PN BC	Other harm	GHG	Score
Fossil						
HS	0[a]	0[a]	– [b]	–[c]	–	−6
LS	+[d]	0[a]	- [b]	-[c]	–	−3
LNG DF	++[d]	+[a,d]	+ [b,d]	– [c]	- (21%)	+1
Carbon-neutral, with renewable hydrogen and CCS/CCU [e]						
e-Methane DF	++[d]	+[a,d]	+ [b,d]	– [c]	+	+3
e-Methanol DF	++[d]	+[a,d]	0[a]	- [c]	+	+3
e-Diesel	++[d]	0[a]	0[a]	0	+	+3
H2-FC/batteries	++[d]	++[d]	++[d]	–[c]	++	+6
Ammonia	*	*	*	*	*	*

LS = $S < 0.1\%$, HS = $S > 0.1\%$.

[a] Available: scrubber, SCR. DPF for sulphur-free fuels = 0.

[b] Developing: methane slip control, particulate filter, ESP. = −1,−2.

[c] PAHs, heavy metals, formaldehyde, methane, infra need = −1, −2.

[d] Low emission without exhaust aftertreatment =+1,+2.

[e] Biofuels, depending on the production process, may resemble respective e-fuels in terms of their environmental impacts.

* Not available at the time of preparing the manuscript. Notably, ammonia as fuel is not expected to emit SO_x, whereas potentially, e.g., N_2O (a strong GHG) may be emitted.

schematic, the scores for the three fuel options are equal, albeit the pros and cons are rated for different issues. Hence, there seems to be no "winning" fuel. All of these fuels can be used in existing engines, if production volumes with carbon-neutral principles grow. Ethanol would also be a feasible fuel for shipping, however, it may remain a fuel for the other transport sectors.

Of fossil fuels, LNG offers a GHG reduction potential of 21%, which is a benefit also for its blending with biomethane or e-methane. Regarding fossil residual and distillate marine fuels, despite the possibilities to reduce harmful exhaust emissions with emission control technologies, carbon-neutrality can be achieved only by using CO_2 capture on-board ships (for CCS/CCU). Demonstrations and consideration of the space requirement are needed to assess the feasibility of this solution in the short-term. Carbon capture on-board ships combined with carbon-neutral fuels would enable very low carbon emissions.

The amount of energy needed in shipping in the future will depend on the fuel savings achieved by operational and technical improvements, e.g., in the design, waste heat recovery, ship size, ship-port interface, new propulsion technologies, alternative maritime routes, regional trade, and modal shifts to rail cargo. The IEA [76] has projected that GHG reductions needed in shipping require halving the energy intensity per travelled distance. Despite energy savings, the energy demand of the maritime sector is projected to remain at the level of approx. 13 EJ (310 Mtoe) in 2050 [76,90,302]. Hence, GHG emissions from shipping need to be tackled substantially by fuel technologies [303]. The magnitude of biofuels available globally is 5 EJ and 3.3 EJ of biofuels was used in the transport sector in 2016, but not in shipping [304,305]. The production of biomethane is projected to increase to 1.7EJ (467 TWh, 40 Mtoe) by 2030 and further to 3.6EJ from the current level (193 TWh) [69]. Although biofuels could be increasingly directed to shipping and aviation along with road-transport switching to batteries, should these fuels meet the RED II or similar requirements, the quantity of compliant fuels likely fall, if new raw materials (lignocellulosic, waste streams) are not utilised. Hence, renewable hydrogen-based e-fuels become interesting for shipping along with the increasingly available renewable electricity.

The outcomes of the projections for the use of marine fuels in the future vary depending on the timeline, considerations of the barriers and competition with other sectors, which further affects the price development. For example, the substantial share of marine fuels in the future has been projected for LNG [303], advanced biofuels [76,90] and e-fuels [306]. Selecting the fuel type depends also on regional boundaries.

This synthesis shows that there is high demand for carbon-neutral fuels, especially those resembling current fossil marine fuels, viz. compatible with proven technologies as "drop-in" fuels (resembling diesel, LNG or methanol). Additionally, harmful exhaust emissions would not need to be compromised. Drop-in fuels are needed for older vessels where retrofitting is less economical, while retrofitting certain diesel engines for methanol use is an option. Many new-build ships have LNG DF or methanol DF engines, which are capable of using two fuels flexibly, increasing the reliability of the fuel supply. The timeline of the potential adaption of these technologies for the main engines of large ships varies:

- Fast-track globally: Diesel-type renewable and e-diesel. *Investments* are needed in fuel production. *Development needs:* e.g., DPF to remove BC and particle number emissions.
- Relatively fast-track globally: Biomethanol or e-methanol retrofits. *Investments* are needed in fuel production, retrofitting of ships and infrastructure. *Development needs:* e.g., DPF to remove particle emissions.
- Moderate timeline, regional: LBG or e-methane: *Investments* needed in fuel production, new ships and infrastructure. *Development needs:* Technologies to remove methane slip and particle emissions.

5.5. Future prospects

The carbon-neutral fuels produced from biomass, waste or from eventually unlimited renewable hydrogen and captured CO_2 are a promise to substantially supplement hydrogen gas technologies, batteries and ammonia in critical transport sectors. Hydrogen gas, ammonia or batteries are not mature for the main means of propulsion for large ships, nor are infrastructure, safety or emission controls for these options widely available for shipping and their feasibility in the long-term is to be seen. Ammonia is reported as a strong marine fuel option [19], however, from a technical point of view, prerequisites to its use as fuel in ships include proven technology to avoid emitting climate warming N_2O.

Preferred solutions for shipping would fit the existing system for practical reasons and in respect of the re-use principle. Carbon-neutral fuels combined with efficient emission control offer drop-in and retrofit options to mitigate GHG and pollutant emissions immediately and simultaneously from many aspects. Fuel molecules themselves do not compete: the methane, methanol, diesel-type or other molecules are acceptable as long as they are carbon-neutral clean fuels and meet sustainability criteria. However, in the short-term, viability of the carbon-neutral raw materials and the production will be limited and hence fossil fuels may be used for a longer time than should, which makes carbon capture on-board ship an interesting option.

Production costs of carbon-neutral fuels are estimated to be lower than the external costs of using fossil fuels, and for drop-in fuels, new infrastructure is not needed for transport and delivery or at the port level. Hydrogen-based e-fuels could become important building blocks in the transport sector where other forms of electrification are difficult. E-fuels could also act as renewable grid storage, hence, accelerating the energy transition to renewables. Choices on marine fuels will be directed largely by other than technical aspects, such as public acceptance, and trust in the fuel availability and prices. Hence, evaluations and solid evidence from many viewpoints are needed to guide non-technical decision-making towards the best choices for the future.

6. Conclusions

Carbon-neutral fuels, including low-carbon and carbon-negative fuels, enabling the use of efficient emission control technologies, could alleviate the climate, health and environmental burden of shipping simultaneously. These would be options for deep-sea shipping and regions where electrification is not feasible. Several technologies are already capable of meeting the present and future shipping emission regulations and with further development enable (near-)zero-emission shipping. Immediate impact can be achieved with solutions fitted into the existing ships (or retrofittable solutions). Marine engines for using diesel-type fuels, methane and methanol are on the market, and so are most emission control technologies needed. Dual-fuel marine engines for methane and methanol have the option to use diesel back-up, and hence safeguards the security of fuel supply. For methanol use, diesel engines can be retrofitted, while for methane new-builds are favoured. Several technology options available allow choices of optimum solutions for different ships, routes and regions.

Carbon-neutral counterparts of fossil marine fuels are bio-, waste- or electro-based fuels, which are feasible as such or as blends (drop-in) up to 100% with fossil fuels. Of the fossil marine fuels, LNG reduces GHG emissions to some extent provided that the methane slip is controlled. However, the main impact on GHG emissions is achieved by replacing (or blending) LNG with LBG or e-methane, and a similar approach applies to carbon-neutral methanol and diesel-type fuels. Sulphur-free carbon-neutral fuels do not emit SO_x and the reduction of NO_x emissions is common with SCR technology. Particles (including BC) can be removed efficiently by filtration when fuels are free from sulphur and ash.

The ship fleet could achieve (near-)zero-emissions, reducing the adverse impacts on the climate, health and environment simultaneously, provided that the production capacity and affordability of carbon-neutral fuels, clean engines and efficient exhaust aftertreatment technologies improve. Substantial investments are needed to introduce these solutions, but also savings are gained with avoided external costs to society caused by the harmful emissions giving arguments to create further support mechanisms and to invest in the clean technologies.

Solutions compatible or retrofittable with the existing ship fleet enabling fast implementation would maximise the impacts as the lifetime of ships is long. Currently, demonstration projects with the participation of public and private stakeholders are needed to examine the most sustainable alternatives for shipping needs. This applies also to potential future options, e.g., hydrogen (fuel cells), ammonia, batteries and wind, to ensure that they do not create new harmful emissions.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.pecs.2022.101055.

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